İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

INTERACTION BETWEEN POLYELECTROLYTES AND LOW MOLECULAR WEIGHT SALTS

M.Sc. Thesis by
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Programme : Chemistry

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POLİELEKTROLİTLERİN KÜÇÜK MOLEKÜL AĞIRLIKLI TUZLARLA ETKİLEŞİMİ

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HAZİRAN 2009

To My Elder Brothers

Yusuf AYDIN and İsmail AYDIN

FOREWORD

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ABBREVIATIONS

I	**:** Ionic Strength
PA	**:** Polyanion
PC	**:** Polycation
PSP	**:** Poly(sodiumphosphate)
PAH	**:** Poly(allylaminehydrochloride)
LMWS	**:** Low Molecular Weight Salt
θ	**:** Degree of Linkage
η_{rd}	**:** Reduced Viscosity
$f(t\ ^{o}C)$	**:** Function of Temperature

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INTERACTION BETWEEN POLYELECTROLYTES AND LOW MOLECULAR WEIGHT SALTS

SUMMARY

Polyelectrolytes are polymers whose repeating units bear an electrolyte group. These groups dissociate in aqueous solutions making the polymers charged. Charged molecular chains, commonly present in soft matter systems, play a fundamental role in determining structure, stability and the interactions of various molecular assemblies.

The unique properties of polyelectrolytes are being exploited in a wide range of technological and industrial fields. One of their major roles, are in the field of biology and biochemistry. Many biological molecules such as polypeptides all proteins and DNA are polyelectrolytes.

They have function as thickeners, emulsifiers, conditioner, flocculants, and they impact surface charge to neutral particles and make them to be dispersed in aqueous solution. They are used in water treatment, in oil recovery, in drug delivery system, in foods, in a variety of materials, including cement.

Recently, polyelectrolytes have been utilized in the production of new type of nanomaterials known as polyelectrolyte multilayers which are obtained using Layer-by-Layer deposition techniques.

Two polyelectrolytes of opposite charges give polyelectrolyte complexes when they are mixed. Polyelectrolyte complexes have major potential applications in membranes, ion exchangers, water purification, textile, battery separators, and in biomedical industries.

The present study attempts to explain general and specific feature of interaction between the given polyelectrolytes with low molecular weight salts that are enables to be model for the unexplained phenomena occuring in biological systems as well as industrial tools for particular purposes.

In this study interaction between poly(sodiumphosphate), poly(allyamine hydrocholoride) and low molecular weight salts such as NaCl, Na_2SO_4, KCl, K_2SO_4 and $CaCl_2$ were investigated.

In the experimental work, interaction with polyions and low molecular salts was followed by conductometric and viscometric measurements depending on the parameters of polyions concentrations, ionic strength, pH and the types of micro cations and anions.

The interaction stoichiometry results in between the polyions and various low molecular weight salts were determined by conductometry and viscometry depending on the ionic strength (constant and varied), pH and polyions concentrations.

Thermodynamic characteristics of equilibrium, ΔG, ΔH, ΔS and lnK were determined using "Degree of linkage" method according to the given parameters. The results were evaluated for the type of binding, binding strength, and thermodynamic data.

Interaction between polyions and low molecular weight salts, in general, did not varied significantly for the polyions, microions concentrations, ionic strength, counterion type and pH. The mol ratio of polyions to various salts was found to be in general, stoichiometric, but the charge ratio deviated from the 1:1 stoichiometry.

Conductometric results showed that interaction between polyions and low molecular weight salts resulted in a charge condensation phenomenon of which comprises the territorial and a small fraction of site binding. Viscometric studies confirmed the conductometric results.

The magnitude of thermodynamic data may give the "degree of screening" in the coulomb interaction system. As a result, negative ΔG values for the given temparatures indicated that the interaction proceeds easily without screening effect of counter ions. Also the increasing values of ΔH and ΔS in the given temperatures reveals that counterions do not perform screening effect. The decreasing values of ΔH and ΔS in the certain range of temperatures shows that significant screening effect of counter ion occurs.

It was concluded that some fractions of coions and counter ions can be distributed either on the open part of coiled polyion(site binding), and can be condensed also onto the free polyion.

However, most of them are distributed around the polyions as an excess charge (territorial binding) equal to but opposite sign of the effective charges of polyions.

POLİELEKTROLİTLERİN KÜÇÜK MOLEKÜL AĞIRLIKLI TUZLARLA ETKİLEŞİMİ

ÖZET

Polielektrolitler, tekrarlanan birimlerinde iyonik gruplar içeren ve elektrolit özellikleri taşıyan polimerlerdir. Bu gruplar sulu çözeltide disosiye olurlar. Korunmasız madde sistemlerinde doğal olarak bulunan yüklü moleküler zincirler, yapıyı, stabiliteyi ve çeşitli moleküler oluşumların girişimlerini tayin etmede temel rol oynarlar.

Polielektrolitler, nadir özelliklerinden dolayı endüstriyel ve teknolojik alanda oldukça yaygın olarak kullanılmaktadır. Başlıca işlevlerinden biri, biyoloji ve biyokimya alanındadır. Polipeptitler, proteinler ve DNA gibi bir çok biyolojik moleküller polielektrolittirler.

Polielektrolitler, dolgu maddesi, emulgatör, ortam koşullarını sağlama, flokulant fonksiyonlarına sahiptir, ve nötral partiküllere yüzey yükü sağlayarak sulu çözeltide dispers olmalarına olanak verir. Polielektrolitler su ve yağların iyileştirilmesinde, ilaç salınım sistemlerinde, gıdada, çimento dahil bir çok malzemelerde kullanılırlar.

Polielektrolitler son zamanlarda Layer-by-Layer depolama tekniği ile elde edilen ve çok tabakalı polielektrolitler olarak bilinen nanomateryallerin elde edilmesinde, yeni uygulama alanı bulmuştur.

Karşı yüklü polielektrolitler birleşerek polielektrolit kompleksleri oluştururlar. Polielektrolit kompleksleri, başlıca membran ve iyon değiştirici olarak suyun saflaştırılmasında, pil ayırıcıları olarak, tekstil ve biyotıp endüstrilerinde kullanılırlar.

Bu çalışmanın amacı, polielektrolitlerin belirli amaçlar için endüstriyel araçlar olarak kullanılmalarının yanında, biyolojik sistemlerdeki açıklanamayan olaylara model oluşturmak üzere küçük molekül ağırlıklı tuzlarla genel ve spesifik girişimlerinin açıklanmasını kapsamaktadır.

Çalışmada, poli(sodyumfosfat) ve poli(allilaminhidroklorür)'ün küçük molekül ağırlıklı tuzlar olan NaCl, Na_2SO_4, KCl, K_2SO_4 ve $CaCl_2$ ile etkileşimleri incelenmiştir.

Deneysel çalışmada, polielektrolitlerin küçük molekül ağırlıklı tuzlarla girişimi, poli iyon ve tuz konsantrasyonları, iyonik şiddet, pH, mikro katyon ve mikro anyon tipi dikkate alınarak iletkenlik ve viskometri yöntemleriyle izlenmiştir.

Poli iyonlar ile çeşitli küçük molekül ağırlıklı tuzlar arasındaki etkileşim stokiyometrisi, iyonik şiddet (I=sabit, I=değişken) pH ve poli iyon konsantrasyonu değişkenlerine bağlı olarak kondüktometrik ve viskometrik olarak belirlenmiştir.

Dengenin termodinamik karakteristikleri, ΔG, ΔH, ΔS ve lnK, seçilen parametrelere göre "bağlanma derecesi" metodu kullanılarak tayin edilmiştir. Sonuçlar, bağlanma tipi, bağlanma kuvveti ve termodinamik verilere dayanarak değerlendirilmiştir.

Poli iyon ve küçük molekül ağırlıklı tuzlar arasındaki etkileşim, poli iyon konsantrasyonu, mikro iyon konsantrasyonu, iyonik şiddet, karşı iyon tipi ve pH'a bağlı olarak önemli derecede değişmemiştir. Poli iyon ve çeşitli tuzlar arasındaki mol oranı genel olarak stokiyometrik bulunmuş, ancak yük oranları 1:1 stokiyometrisinden sapma göstermiştir.

İletkenlik sonuçları, poli iyonlarla küçük molekül ağırlıklı tuzların girişiminin "çevresel bağlanma (territorial binding)" ve küçük bir fraksiyonunda "lokal bağlanma (site binding)" yı kapsayan yük kondensasyonu olduğunu göstermiştir.

Termodinamik veriler, kulom girişim sistemindeki "perdeleme derecesini" vermektedir. Belirli sıcaklıklardaki ΔG değerleri reaksiyonun kendiliğinden yürüdüğünü ve artan ΔH ve ΔS değerleri karşı iyonların "perdeleme etkisi" yapmadığını, ancak belirli sıcaklık aralığında azalan ΔH ve ΔS değerleri karşı iyonların önemli derecede "perdeleme etkisi" yaptığını göstermektedir.

Sonuçlar yorumlandığında, birleşen ve karşı iyonların belirli bir fraksiyonunun sarmal poli iyonun açık kısımlarında "lokal bağlanma (site binding)" yaparak poli iyon üzerinde, ve önemli bir fraksiyonunun poli iyon etrafında aşırı karşı yük olarak "çevresel bağlanma (territorial binding)" ile dağılarak kondense olduğu görüşüne varılmıştır.

1. INTRODUCTION

The interaction of synthetic polyelectrolytes with low molecular weight salts in aqueous solution depending on different parameters has been expected to provide a model for understanding of structural properties and reactions of natural polyions in living organism, and to contribute the related theories [1, 2, 3] as well. Knowledge of polyelectrolyte aqueous solution properties are very important because of their uses in industrial area and environmental applications.

In the last two decades intensive studies on polyelectrolytes reactions with microions has been carried out to explain the main specific feature of coulombic interactions, and efforts has been made to complete the missing part of the given theories according to the results of new experimental studies involving different polyelectrolytes and certain salts of representative and transition elements [4, 5, 6, 7].

The polyelectrolyte as polyanion used in this study is sodium(polyphosphate) which is one of the few anionic inorganic polyelectrolyte. Sodium(polyphosphate) as polyelectrolytes and polyelectrolyte complexes has been studied by T. TULUN et al. [8, 9, 10].

The poly(allylaminehydrocholoride) as polycation is a water soluble polyelectrolyte about which it was not encountered any particular references in the literature. As a matter of fact, there are very few studies related with the interaction between polycations and low molecular weight salts [6].

It has been hoped that the results of this study might contribute to the scientists working on polyelectrolyte properties.

2. THEORETICAL PART

2.1 Polyelectrolytes [11]

A polyelectrolyte is a macromolecular species that upon being put in water or any other ionizing solvents dissociates into highly charged polymeric molecule. The dissociation is accompanied by smaller oppositely charged counter ions that naturalize the charge on the repeating units of polyelectrolyte. A polyelectrolyte, in low ionic strength solutions tends to be in its most extended and uncoiled form due to the intramoleculer repulsion of the unscreened charges on each monomeric unit. On the contrary, when the ionic strength of the solution is increased a polyelectrolyte tends to become more coiled due to the screening effects of charges by the excessive presence of counter ions and low molecular weight salt in the solution [12]

Many biological molecules are polyelectrolyte. For instance, polypeptides, proteins and DNA are polyelectrolytes. Both natural and synthetic polyelectrolytes are used in variety of industries [16].

Polyelectrolytes can be strong and weak types. A strong polyelectrolyte dissociates completely in solution for most reasonable pH values. A weak polyelectrolyte has dissociation constant in the range of ~2 to ~10 meaning that it is partially dissociated at intermediate pH values. The functional charges of polyelectrolytes can be modified by changing the solution pH, counter ion concentration, ionic strength etc. The degree of changing is one of the main factor affecting properties of polyelectrolyte. Counter ions released from polyelectrolyte and low molecular weight salt affects the ionic strength of the solution. This in turn affects other properties, such as electrical conductivity. The mutual repulsion of the polyion and counter ions cause the expansion of the chain. The ionic charges attach to the chain create a regions of high density so that affecting the activity coefficients and properties of counter and micro ions in these localities. [14].

Polyelectrolytes can be cationic and anionic in their polymer unit. If the polyion is positively charged, it is called cationic polyelectrolyte, and when the polyion is negatively charged it is called anionic polyelectrolyte.

2.1.1 Condensed linear polyphosphates

Condensed phosphates, in general, are formed by repeated condensation polymerization of tetrahedral [PO_4] units. The overall formula of condensed phosphates consisting of either straight (lineer) or branched chain is given by the formula $M_{n+2}P_nO_{3n+1}$. This formula applies to the homologous series of condensed phosphates.

Condensed phosphates are divided three major categories: linear polyphosphates, ring (cyclo) phosphate (metaphosphates) and ultraphosphates (crosslinked condensed phosphates). When the number of units in the polymeric molecule becomes very large (n=50 to 200) the formula is given in the (PO3 $)_n^{n-}$ form which refers to a ring formation, and called metaphosphate. The ring phosphate composition form well-crystallized salts [19].

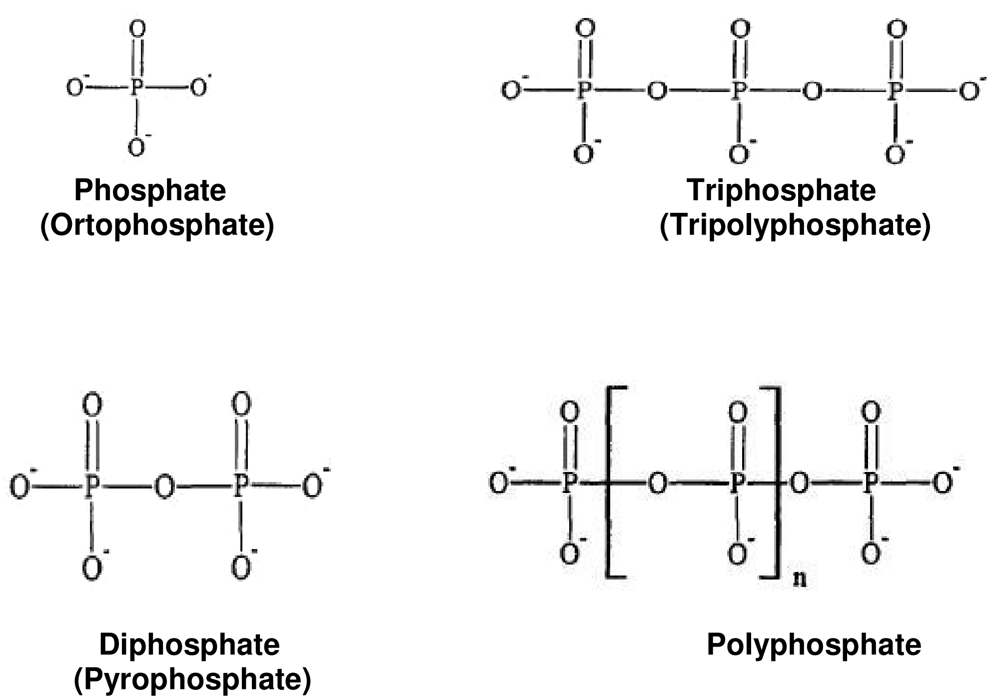


Figure 2. 1: Linear polyphosphate

Linear polyphosphates[figure 2.1] are the salts of linear polyphosphoric acid. Alkali and alkaline earth polyphosphate salts have been most studied because of their uses in many fields. The basic unit is the (PO_4^{3-}), and it is the first member of the chain series, with di- and triphosphate being the second and the third members, respectively.

Linear polyphosphates with intermediate chain lengths (n= 10 ~ 50) can usually be obtained in the glassy form [19]. The average chain length, as measured by the number of phosphorous atoms per chain(repeated unit is the (PO_3^{3-}), can range from 3 to 3000.

Poly(sodiumphosphate) subjected to this study is one of the member of chain polyphosphates having linear polydisperse polyelectrolyte nature with average degrees of polymerization ranging up to 20.

For several reasons, the polyphosphates are ideally suited for the study of polyelectrolyte behavior [17]

1. They are easily prepared to a degree of purity.
2. Molecular weight distribution function has been determined both theoretically and experimentally so that results obtained with unfractionated samples by different experimental methods can be correlated.
3. The viscosity behavior is uncomplicated because polyphosphate chains are unbranched.

Poly(sodiumphosphate) is prepared in many ways by condensation polymerization procedures at 650 ^{o}C and water soluble glassy compound are obtained.

Poly(sodiumphosphate) in aqueous solutions of low ionic strength are capable forming complexes with other polymers, especially proteins, basic polypeptides and nucleic acids. Their ability increases as the chain length of polyphosphate molecule increases.

Poly(sodiumphosphates) as well as other linear chain phosphates possess properties very similar to those of cross-linked, solid ion exchange resin (Thilo, 1955).

The behavior of polyphosphates as dissolved ion exchange agents is evidence of their ability to form complexes with counter ions.

Polyphosphates are very good complexing agents for metal ions. This property is widely exploited in the fractionation of polyphosphates, and for other analytical purposes. The chemical and phsico-chemical properties of the inorganic polyphosphates will facilitate the development and use of efficient and reliable biochemical procedures for isolation, purification, identification and determination of polyphosphates during their extraction from the alive cell.

2.1.2 Polyelectrolyte interaction with low molecular weight Salts

The characteristic reaction of polyelectrolyte in aqueous solution is namely electrolytic dissociation and electrostatic association depending on the polyelectrolyte concentration. Experimental studies showed that most of the polyelectrolytes can give reaction only in narrow concentration range. The charge density of polyelectrolytes can be reduced, to an extent, by low molecular salts through the reactions of ion–binding, ion fixation or ion association. Polyelectrolytes in dilute aqueous solution are found loosely and they are accepted as rod–like depending on the degree of dilution. In the relatively concentrated salt free and salt solution they are spherical coils [figure 2.2].

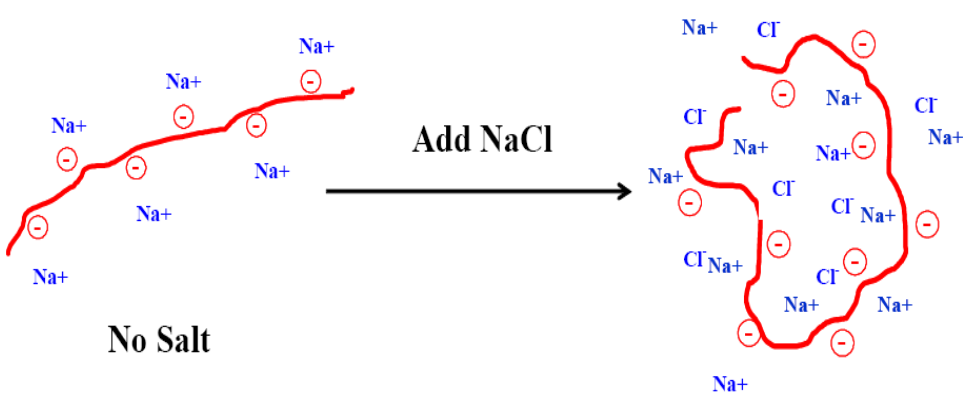


Figure 2. 2: The shape of polyelectrolyte molecule in salt and salt free solution

A number of attempts have been made for the theoretical explaination on the interaction between the polyelectrolyte and low molecular weight salts in aqueous solution; because of the simple Debye-Huckel theory is unacceptable when the charge density of polyelectrolyte is large.

The counter ion binding theory given by Manning [1, 2, 3] has been found of relatively high utility, but in the case of the high charge density of polyelectrolyte, it can not be applied satisfactorily. It is because of the two different kind of counter ion binding can proceed in the solution. Some of the counter ions (micro ions) are attracted to a volume part of polyelectrolyte domain by electrostatic interaction. These micro ions are mobile to an extent, and the binding is called "Diffuse or territorial binding''. The rest of the micro ions are attracted by functional groups of polyelectrolyte for giving ion-pairs, and localized on the polyelectrolyte backbone. This type of binding is referred as "Site binding (or localized binding)". In the result one of these binding types can predominate in the medium.

Manning's condensation theory predict that when charge density on polyelectrolyte (polyion) larger than a critical charge density which is a unity, counter ions or (micro ions) condense (bind) onto the polyion until these two charge densities are equal. The rest of the micro ions are localized in the polyion ionic atmosphere.

Nordmerer [4] showed that there was significant deviation between experimental results and the "Condensation Theory" when the critical charge density is smaller than unity. Satisfactory agreement exist with the theory, only, when the critical charge density in higher than unity.

2.1.3 Conductivity of polyelectrolytes

Polyelectrolyte solutions show large conductance. Conductivity measurements give further information on the nature of polyelectrolyte solution. Conductance of solution increases when dielectric constant of medium increases because of the mobile counter ions found in the electrostatic field of polyelectrolyte freely moves to increase the net charge on the polyelectrolyte.

Conductance or specific and equivalent conductivity are directly reflect the electric transport of micro ions (low molecular mass). However this phenomenon do not truly reveal the transport of counter ions released from polyions. Small ions influence the flexibility of polyion chains.

2.1.4 Polyelectrolyte applications

Polyelectrolytes have found a number of important applications in the major fields of science and engineering such as chemistry, physics, biology, chemical and materials engineering in addition to essential functions of natural polyelectrolytes in human physiology and cellular mechanisms in the form of proteins, polypetides and nucleic acids. Their applications in chemistry are mainly centered at the interface of polymer materials, colloids, surface and analytical chemistry. Recently, polyelectrolytes have found extensive use in a variety of nano projects and technologies both in the academic and the industrial research and development areas [12].

Polyelectrolytes have been used in the health and personal care industry as thickening reagents, rheology modifiers and viscosity enhancers for shampoos, conditioners, deodorants and body lotions they have also been used in water treatment, waste treatment, sludge dewatering and the pulp and paper industry as retention aids as well as flocculating and coagulating agents for solid-liquid separations [12, 19].

Other polyelectrolytes are as used additives to alter the physical properties of aqueous products.

One of the most important properties of polyelectrolytes is their complexation when mixed with other polyelectrolytes of opposite charge, and as a result they give polyelectrolyte complexes. The interaction of two polyeletrolytes depends on the characteristics of interacting groups. An integral type of polyelectrolyte complex is obtained when the interacting group is on the main chain or pendant type polyelectrolyte complex result in if the interacting group is on the side chain [12, 18].

Depending on the experimental conditions a polyelectrolyte complex can be

a. complex gel which are croslinked network in nature,
b. a polysalt which are, in special case, thin films at interface,
c. remain in solutions as aggregates without significant phase separation.

The bond strength between two polyelectrolytes can be gained by, mainly, electrostatic and hydrophobic interactions, in special case by hydrogen bonding.

Major potential applications [15] of PEC can be membranes (for desalination and ultrafiltration), ion exchangers. They are used in water purification, environmental and textile industries, separation anionic complexes of transition metal ions, separation of hazardous minerals from body fluids, battery separators,biomedical, contact lenses and artificial kidneys.

Recently, polyelectrolytes in opposite signs can be assembled to give thin films as polyelectrolyte complex using layer-by-layer method which is mentioned by Iler in 1966, but expanded and introduced as new layer-by-layer method by Decher[13]. As a result, a reproducible deposition or build up of polyelectrolyte complexes can be obtained on different substrates, and find applications in different fields.

Polyelectrolyte complexes and polyelectrolyle multilayers share similar physical and chemical properties in terms of their internal and, physical structures and morphology.

3. EXPERIMENTAL PART

3.1 Chemicals

Commercially available poly(sodiumphosphate) (Sigma-Aldrich, M_w= 101.96g/mol CAS No:68915-31-1) was utilized as polyanion, Poly(allylaminehydrochloride) (Alfa Aesar, M_w= 93.56 CAS=71550-12-4) as polycation. Potassium chloride (merck), Potassium sulfate (merck), sodium sulfate (carlo erba), sodium chloride (merck), calcium chloride (merck), percholoric acid (merck) were used.

3.2 Methods

The methods chosen for this study were mainly conductometry and viscometry. The stochiometry of interaction were determined by conductometric titration and viscometry methods. Molecular weight determinations of polyions were carried out using viscometry and wet chemistry methods. In addition, for the thermodynamic data "Degree of Linkage" method was used.

3.3 Solutions

All solutions were freshly prepared for a week period

$1x10^{-1}$ M $(NaPO_3)_n$

2.55 g $(NaPO_3)_n$ is dissolved in necessary amount of water and the diluted to 250mL with distilled water (stock solution).

$1x10^{-1}$ M $(NaPO_3)_n$ (I=1 M)

2.55 g of $(NaPO3)_n$ is dissolved in necessary amount of 1M $HClO_4$ and then diluted to 250ml with 1M $HClO_4$ solutions (stock solutions)

$1x10^{-1}$ M Poly(allylaminehydrochloride) (PAH)

0.935 g of PAH is dissolved 100 ml of distilled water

$1x10^{-1}$ M Poly(allylaminehydrochloride) (PAH) (I=1 M)

0.935 g PAH is dissolved in necessary amount of 1 M $HClO_4$ solution, then diluted to 100 ml with 1 M $HClO_4$ solution

1 M NaCl

14.62 g of NaCl is dissolved in 250 ml of distilled water (stock solution)

$1x10^{-1}$ M NaCl (I= 1M)

1.46 g NaCl is dissolved in necessary amount of 1 M $HClO_4$ solution, then diluted to 250 ml with 1 M $HClO_4$ solution

1M Na_2SO_4

35.51 g Na_2SO_4 is dissolved in 250 ml of distilled water

$1x10^{-1}$ M Na_2SO_4 (I=1M)

3.55 g Na_2SO_4 is dissolved in necessary amount of 1 M $HClO_4$ and then diluted 250ml with 1 M $HClO_4$ solution.

1 M KCl

18.64 g KCl is dissolved in 250 ml of distilled water.

$1x10^{-2}$ M KCl (I=$1x10^{-1}$ M)

0.186 g KCl is dissolved in necessary amount of $1x10^{-1}$ M $HClO_4$ and then diluted 250 ml with $1x10^{-1}$ M $HClO_4$ solution.

1 M K_2SO_4

43.57 g K_2SO_4 dissolved in 250 ml of distilled water.

$1x10^{-2}$ M K_2SO_4 ($I=1x10^{-1}$M)

0.436 g K_2SO_4 dissolved in necessary amount of $1x10^{-1}$ M $HClO_4$ and then diluted to 250 ml with 10^{-1} M $HClO_4$ solution.

1 M $CaCl_2$

11.1 g $CaCl_2$ dissolved in 100 ml of distilled water.

$1x10^{-1}$ M $CaCl_2$ (I= 1M)

1.11 g $CaCl_2$ dissolved in necessary amount of 1 M $HClO_4$ and then diluted to 100 ml with 1 M $HClO_4$ solution.

1M $HClO_4$

27.5 mL of $HClO_4$ (d=1.54 g/mL, 60% (w/w)) is diluted to 250 mL of distilled water

3.4 Equipments

The following instruments were used in measurements
Conductometr, Inolab WTW
pH meter, Jenway 3040 Ion Analyser
Viscosimetr, Ostwald
Thermostat, P Selecta(Spain)
Stirrer, IKAMAG
Perkin Elmer IR spectrometer one

3.5 Experiments

3.5.1 Moleculer weight determination of polyions

Molecular weight of PSP and PAH were carried out by viscosimetry. In addition, molecular weight of PSP was also determined by end group titration method.

3.5.1.1 Molecular weight determination of poly(sodiumphosphate) by end group titration

0.5 g of polysodium phosphate was dissolved in 100 mL of water and pH was lowered to about 3 using HCI (1 M) and then titrated potentiometrically with standart NaOH (0.05 M) solution until the pH value of 4,5 and number of mL equivalents of base, A mL, consumed until the first end point was determined. The total phosphorus amount of the phosphate was determined in another poly(sodiumphosphate) sample of the same weight after a complete hydrolysis procedure. The complete reversion of the polyphosphate to the orthophosphate form can be achieved by gently boiling the sample in a HNO_3 (1 M) solution for three hours under reflux then, pH was lowered to about 3 and the solution was titrated potentiometrically with 0.05M standart NaOH solution until the pH value of 4,5 and the procedure was continued beyond the second end point at about pH, 9 and the number of mili equivalents of base, A_h mL, consumed between two end points were determined.

Titration curves of $(NaPO_3)_n$ before and after hydrolysis are given in in Figure 3.1. and 3.2.

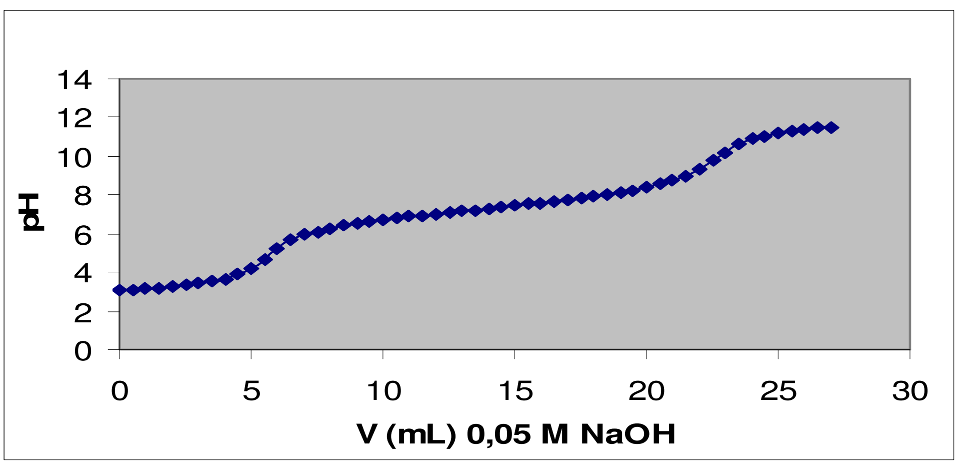


Figure 3. 1: Titration curve of $(NaPO3)_n$ before hydrolysis

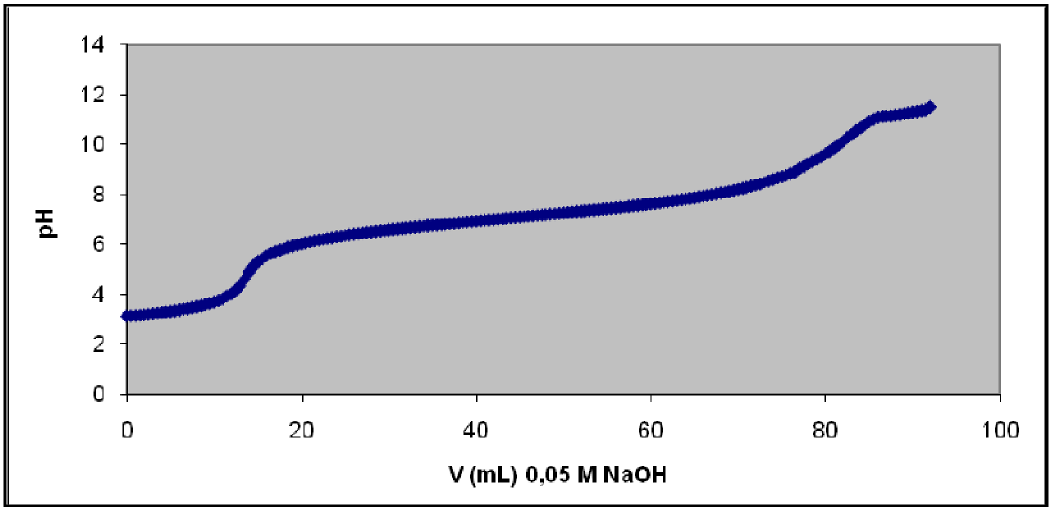


Figure 3. 2: Titration curve of $(NaPO_3)_n$ after hydrolysis

Finally P_2O_5 % (End Group) and P_2O_5 (Total) were calculated (Table 3.1).

$$\%P_2O_5(endgroup) = \frac{A}{A_h} x100 \tag{3.1}$$

$$\frac{P_2O_5(total)}{P_2O_5(endgroup)} = \frac{n}{2} = \frac{A_h}{A} \tag{3.2}$$

Table 3. 1 : The results of end group titration

Titration Procedure	Added NaOH (V mL)	$\%P_2O_5$
Before Hydrolysis (end group)	5.5	8.33
After Hydrolysis (total)	66.0	99.96
n =24 Molecular Weight = 2447.04 g/mol		

3.5.1.2 Molecular weight determination of poly(sodiumphosphate) by viscometry

Solution viscosity is basically a measure of the size of polymer molecules and it is emprically related to molecular weight of polymers. Thus, viscosity measurement constitues an extremely valuable tool for the molecular characterization of polymer. Dilute solution viscosity is usually measured in capillary viscometer of the Ostwald or Ubbelohde type and concentration, C, is expressed in grams per desiliter (g/dL,g/l00 mL). Measurements of solution viscosity are usually made by comparing the efflux time, t, required for a specific volume of polymer solution to flow through a capillary tube with the corresponding efflux time, t_0, for the solvent. From t_0, and the solute concentration,C, the following equations are derived [20, 21]

RelativeViscosity	$\eta_r = t/to$	**(3.3)**
Spesific Viscosity	$\eta_{sp} = \dfrac{t - to}{to} = \eta_r - 1$	**(3.4)**
Reduced Viscosity	$\eta_{red} = \eta_{sp} / C$	**(3.5)**
Intrinsic Viscosity	$[\eta] = (\eta_{sp}/C)_{C=0}$	**(3.6)**

The molecular weights of linear polyions were calculated from the intrinsic viscosity of the solution by the following Mark Houwink equation:

$$[\eta] = K\ M^a \qquad \textbf{(3.7)}$$

In this equation a and K are constants and dependent to the temperature, type of solvent and polymer and M represents the molecular weight.

In these measurements Ostwald type viscometry is used. Viscosity measurements of poly(sodiumphosphate) were carried out in 0.035 M NaBr solution at 25.5^{o}C. Results are given in Table 3.2. and Figure 3.3.

Table 3. 2 : Viscosity values for poly(sodiumphosphate) ($K=69x10^{-5}$ dL/g, a=0.61)

$(NaPO_3)_n$ C (g/dl)	t (min.)	t (s)	η_r	η_{sp}	$\eta_{red} = \eta_{sp}/C$
0.3087	1.257	75.42	1.016	0.016	0.052
0.3704	1.255	75.3	1.015	0.015	0.039
0.4630	1.251	75.06	1.011	0.011	0.024
0.6173	1.245	74.7	1.006	0.006	0.010
0.9260	1.245	74.7	1.006	0.006	0.007
NaBr	1.237	74.22			

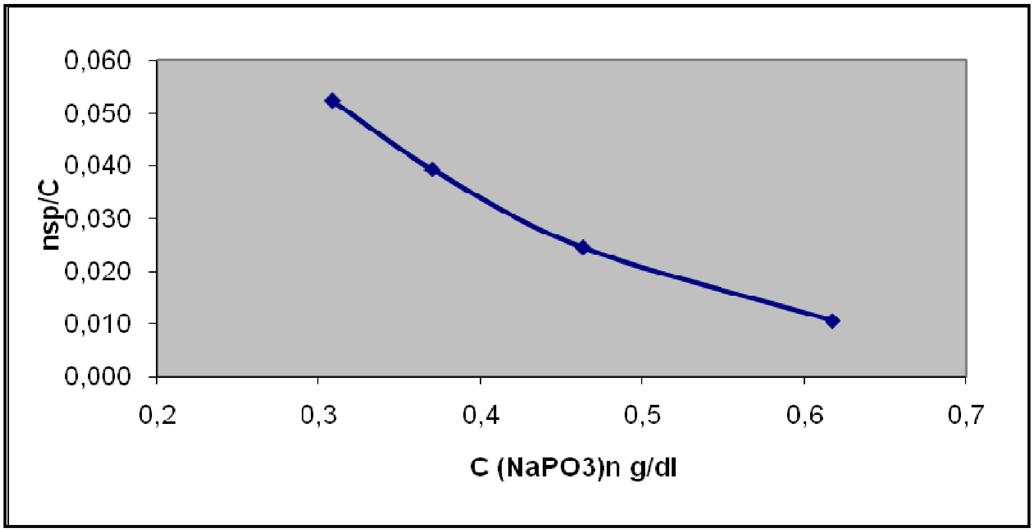
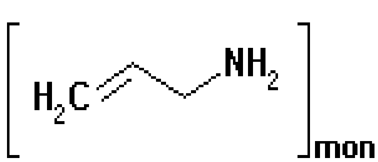


Figure 3. 3: Viscosity curve for poly(sodiumphosphate)

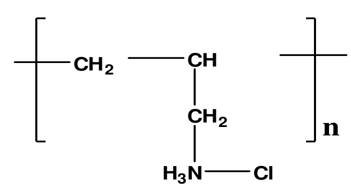
The molecular weight of $(NaPO_3)n$ was found as 2936.69 g/mol by using the equation 3.7

3.5.1.3 Molecular weight determinaion of polly(allylaminehydrochloride) by viscometry

Viscosity measurements of Poly(allylaminehydrochloride) are done in 0.5 M NaCl solution at 25°C. Results are given in Table 3.3. and Figure 3.4.



Poly(allylamine)



Polly(allylaminehydrochloride)

Table 3. 3: Viscosity values for poly(allylaminehydrochloride)

($K=7{,}19x10^{-5}$ dL/g, a=0,794)

PAH C (g/dl)	t (min.)	t (s)	η_r	η_{sp}	$\eta_{red} = \eta_{sp}/C$
0.33	1.449	86.94	1.15	0.15	0.45
0.40	1.493	89.58	1.18	0.18	0.46
0.50	1.559	93.54	1.24	0.24	0.47
0.67	2.074	124.44	1.64	0.64	0.96
1.00	2.336	140.16	1.85	0.85	0.85
NaCl	1.262	75.72			

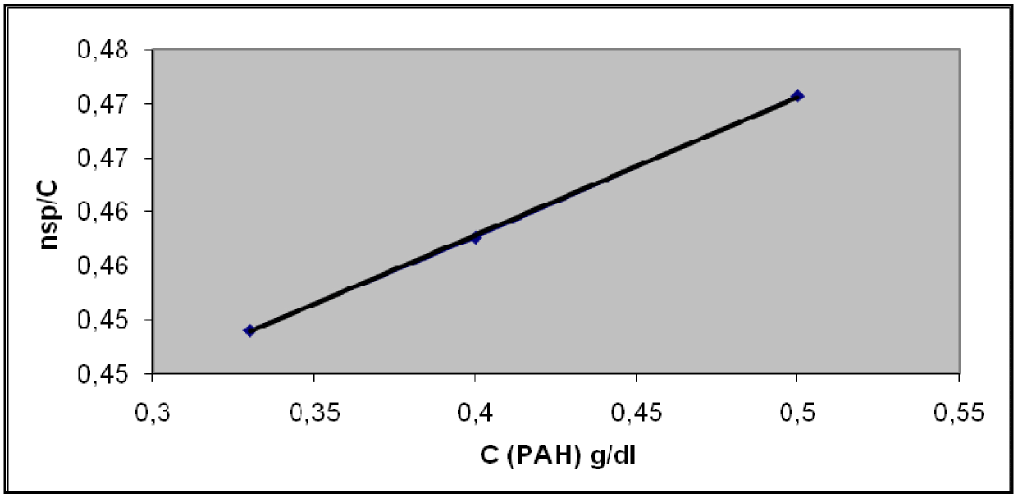


Figure 3. 4: Viscosity curve for PAH

The molecular weight of PAH was found as 52242.94 g/mol by using the equation 3.7.

3.5.2 Determination of equivalent weight of polyions

3.5.2.1 Determination of equivalent weight of poly(sodiumphosphate)

Equivalent weight of poly(sodiumphosphate),$(NaPO_3)_n$, was determined by alkalimetry after poly(sodiumphosphate) has been converted to its acid form, $(HPO_3)_n$, by ion exchange method using Amberlite IR-120 (strong acid cation exchanger).

Ion Exchange Column : 15g of resin was weighed and put in distilled water and let to stand overnight. After decantation of water, 3M HCl was added, and then it was shaked and filtered. Acid treatment was repeated for three times and washed with large amount of water.

Cation and anion exchangers were kept in 1M HCl and in 0.5M NaOH recpectively for three hours, and then they are washed several times with water. The 2/3 part of column was filled with the exchangers.In addition, cation exchange column was treated with 150 mL 1 N HCl,and then excess of alkali from anion exchanger column and excess of acids from cation exchanger column were removed by distilled water.

Column lenght: 50 cm, diameter: 1cm, flow rate:1.5mL/min, efficiencies of anion and cation exchange column are 98.9% and 98.5% respectively.

The eluate (HPO3)n was titrated with standard 0.05M NaOH volumetrically by using methyl orange indicator. The calculated equivalent weight of Poly(sodiumphosphate) is 100.46 g eqw [22].

3.5.2.2 Determination of equivalent weight of poly(allyaminehydrochloride)

Equivalent Weight of PAH was determined by argentimetry and found as 94.50 g eqw.

3.5.3 Stoichiometric determinations

3.5.3.1 Conductometric titration method

Solutions of electrolytes conduct an electric current by the migration of ions under the influence of an electric field. Like a metallic conductor, they obey Ohm's law. Exceptions to this law occur only under abnormal conditions—for example, very high voltages or high-frequency currents. Thus, for an applied electromotive force *E,* maintained constant but at a value which exceeds the decomposition voltage of the electrolyte, the current *i* flowing between the electrodes immersed in the electrolyte will vary inversely with the resistance of the electrolyte solution, R. The reciprocal of the resistance, *1/R,* is called the conductance, L, and is expressed in reciprocal ohms, or mhos.

The standard unit of conductance is specific conductance, χ, which is the conductance in mhos of one cubic centimeter of solution between two electrodes in one centimeter square and one centimeter apart. The observed conductance L of a solution depends inversely on the distance l between the electrodes and directly upon their area S, cm^2

Specific Resistance, $r = R \text{ ohm} \times S \text{ cm}^2 / 1 \text{ cm}$ **(3.8)**

$1 / r = \chi$ specific conductance = conductivity **(3.9)**

$\chi = (1 / R \text{ ohm}^{-1}) x (l \text{ cm} / S \text{ cm}^2)$ **(3.10)**

$\chi = \text{ohm}^{-1} \times \text{cm}^{-1} = K \text{ cm}^{-1} \times L \text{ ohm}^{-1}$ **(3.11)**

where $K \text{ cm}^{-1}$ is the coefficient related wth the instrument and

$\chi = \text{ohm}^{-1} \times \text{cm}^{-1}$ = Siemens

The electrical conductance of a solution is the summation of all the ions present in the solution. It depends upon the number of ions per unit volume of the solution and upon the velocities with which these ions move under the influence of the applied electromotive force. The specific conductance, χ,decreases when electrolyte solution is diluted.

Fewer ions to carry the electric current are present in each cubic centimeter of solution. However, in order to express the ability of individual ions to conduct, a function called the equivalent conductance is needed. If C is the concentration of the solution in gram equivalents per liter, then the volume of solution in cubic centimeters per equivalent is equal to 1000/C, so that,

$\Lambda = 1000 \chi / C$ **(3.12)**

Conductometric titration of PSP and PAH with different salts were carried out for different polyanion/polycation and salt concentrations in ionic strength varied and ionic strength constant solution in the possible concentration range. Results are given in Table 3.4, Table 3.5 and Appendix A (Figure A.1 – A.36)

Table 3. 4: Results of conductometric titration of PSP with different salt solution (I= Varied)

Solution	Titrant	$(NaPO_3)n$ / Salt Ratio				
$(NaPO_3)n$ (mol/L)	Salt (mol/ L)	NaCl	Na_2SO_4	KCl	K_2SO_4	$CaCl_2$
$1x10^{-1}$	$1x10^{-1}$	1:0.9	1:0.9	1:1	1:1	1:1.1
$1x10^{-2}$	$1x10^{-2}$	1:1.2	1:1	1:1.2	1:1.2	1:1.5
$1x10^{-3}$	$1x10^{-3}$	1:1	1:1	1:1	1:1	1:1.7
$1x10^{-4}$	$1x10^{-4}$	1:1	1:1	1:1	1:0.7	1:1

Table 3. 5: Results of conductometric titration of PSP with different salt solution (I= Constant)

	Solution	Titrant	$(NaPO_3)n$ / Salt Ratio				
Ionic Strenght	$(NaPO_3)n$ (mol/L)	Salt (mol/ L)	NaCl	Na_2SO_4	KCl	K_2SO_4	$CaCl_2$
1	$1x10^{-1}$	$1x10^{-1}$	1:1	1:1	-	-	1:1.1
$1x10^{-1}$	$1x10^{-2}$	$1x10^{-2}$	1:1	1:1.4	1:1.6	1:1.6	1:1.5
$1x10^{-2}$	$1x10^{-3}$	$1x10^{-3}$	1:1.5	1:1	-	1:1.2	1:1
$1x10^{-3}$	$1x10^{-4}$	$1x10^{-4}$	1:0.9	1:0.8	1:2	1:1.4	1:0.9

The results of Poly(allylaminehydrochloride) (PAH) –and various Salt stoichiometry were given in Table 3.6, Table 3.7 and Appendix A (Figures A.37 – A.74)

Table 3. 6: Results of conductometric titration of PAH with different salt solution (I= Varied)

Solution	Titrant	$(NaPO_3)n$ / Salt Ratio				
(PAH) (mol/L)	Salt (mol/ L)	NaCl	Na_2SO_4	KCl	K_2SO_4	$CaCl_2$
$1x10^{-1}$	$1x10^{-1}$	1:1.2	1:1.2	1:1.2	1:1	1:1
$1x10^{-2}$	$1x10^{-2}$	1:1	1:1	1:1.2	1:1.2	1:1
$1x10^{-3}$	$1x10^{-3}$	1:1.2	1:1.4	1:1	1:1.4	1:1
$1x10^{-4}$	$1x10^{-4}$	1:1	1:1.2	1:1	1:1.2	1:1

Table 3. 7: Results of conductometric titration of PAH with different salt solution (I= Constant)

	Solution	**Titrant**	**(PAH) / Salt Ratio**				
Ionic Strenght	(PAH) (mol/L)	Salt (mol/ L)	NaCl	Na_2SO_4	KCl	K_2SO_4	$CaCl_2$
1	$1x10^{-1}$	$1x10^{-1}$	1:0,8	1:1.3	-	-	1:1.8
$1x10^{-1}$	$1x10^{-2}$	$1x10^{-2}$	1:0.7	1:0.7	1:0.9	-	1:1.5
$1x10^{-2}$	$1x10^{-3}$	$1x10^{-3}$	1:1	1:1	-	1:0.9	1:1.6
$1x10^{-3}$	$1x10^{-4}$	$1x10^{-4}$	1:1	1:1.5	1:1.3	1:2	1:1

The table 3.8 given below (curves in Appendix A(Figures A.75 – A.84) are related with charge ratios for the PSP-Salt systems.The PSP and salt solutions were prepared at a concentration that is related with equivalent charges.

Table 3. 8 : Charge ratios of PSP with various salts

Solution	Salt	PSP:Salt Charge Ratios, [-/+]	
		(I=varied)	(I=$1x10^{-2}$mol/L)
0.102 mg/mL PSP	0.102 mg/mL NaCl	1:1.7	1:1.7
0.142 mg/mL PSP	0.142 mg/mL Na_2SO_4	1:1.4	1:1.4
0.102 mg/mL PSP	0.102 mg/mL KCl	1:1.4	1:1.4
0.174 mg/mL PSP	0.174 mg/mL K_2SO_4	1:1.2	1:1.2
0.219 mg/mL PSP	0.219 mg/mL $CaCl_2$	1:1.1	1:1.1

The results of Titrations of $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L NaCl and KCl in varied pH values at 25^{o}C are given in the following figures.

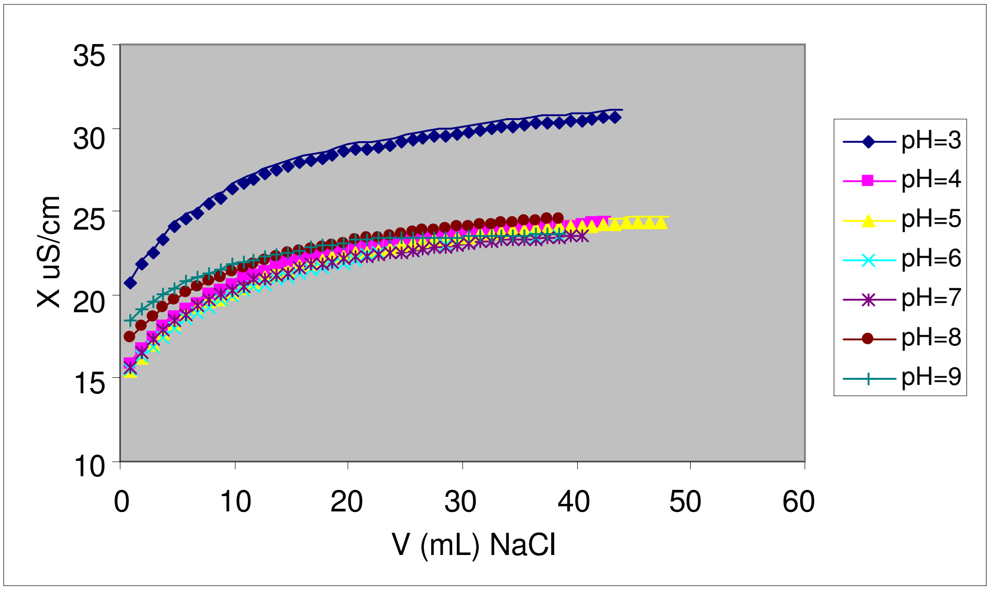


Figure 3. 5: $\chi = f$(ml titrant) curve in varied pH values for $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L NaCl

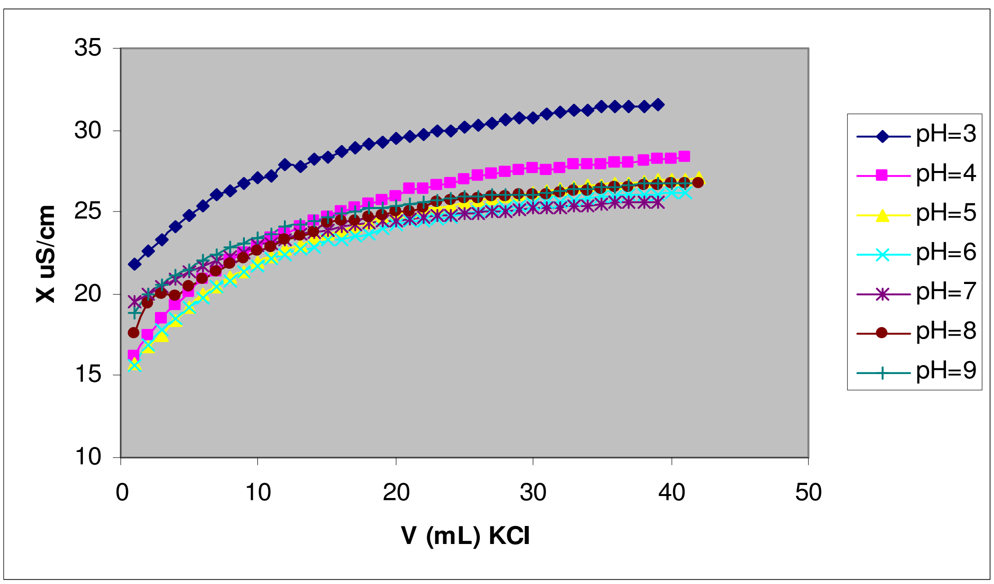


Figure 3. 6: $\chi = f$(ml titrant) curve in varied pH values for $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L KCl

3.5.3.2 Viscometric determination

In this part of the study, viscosity measurements of Salts, PSP, PAH, PSP-Salt and PAH-salt solutions were carried out as a function of mol ratio and pH for both I=varied and I=constant solutions at 25^0C [23, 24].

Viscosities values for dilute solutions of NaCl (C_{NaCl}=0.01g/dl) and PSP mixtures in different mol ratios were given in Table 3.9 and Figure 3.7.

Table 3. 9: Viscosity values for 0.01g/dl NaCl +1,71x10^{-3}mol/L PSP

Mol ratio NaCl/PSP	t (s)	relative viscosity $t/t_o=n_r$	specific viscosity $nr-1=n_{sp}$	reduced viscosity $n_{sp}/C=n_{red}$
0	72.4	1.001	0.001	0.166
0.11	72.56	1.004	0.004	0.387
0.25	72.52	1.003	0.003	0.332
0.43	72.36	1.001	0.001	0.111
0.54	72.44	1.002	0.002	0.221
0.67	72.56	1.004	0.003	0.387
0.82	72.68	1.005	0.005	0.553
1.00	72.56	1.004	0.004	0.387
1.22	72.56	1.004	0.004	0.387
1.50	72.56	1.004	0.004	0.387
1.86	72.44	1.002	0.002	0.221
solvent	72.28	1	0	

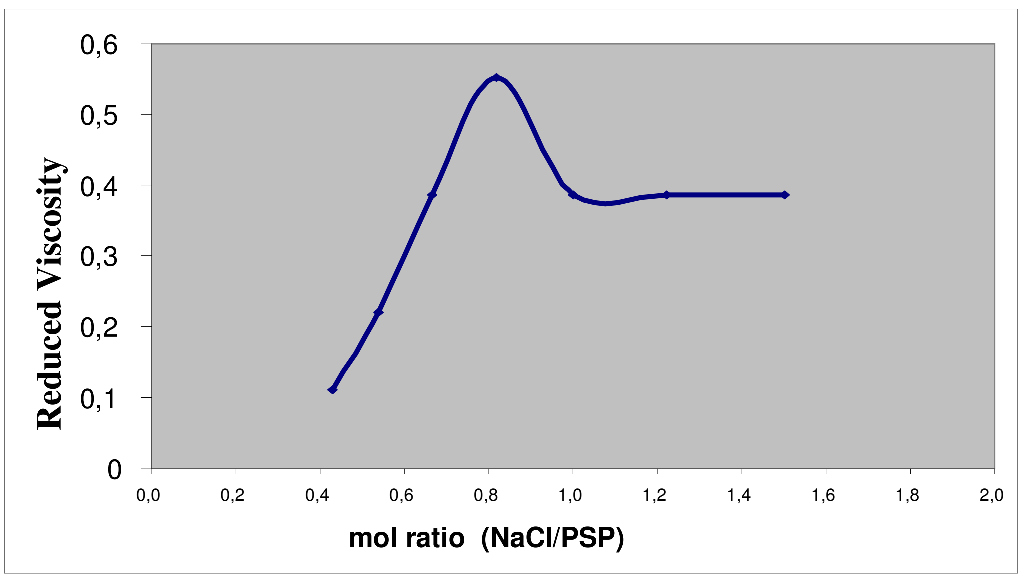


Figure 3. 7: Viscosity curve for 0.01g/dl NaCl + 1.71x10^{-3} mol/L $(NaPO_3)n$

Table 3. 10: Viscosity values in different mol ratio of $1x10^{-2}$ mol/L various salt + $1x10^{-2}$mol/L PSP ($I=1x10^{-1}$ M)

Mol ratio Salt/PSP	reduced viscosity NaCl/PSP	reduced viscosity Na_2SO_4/PSP	reduced viscosity KCl/PSP	reduced viscosity K_2SO_4/PSP
0		0.082	0.117	0.047
0.11	0.001	0.082	0.116	0.103
0.25	0.014	0.073	0.124	0.093
0.43	0.011	0.065	0.093	0.080
0.67	0.007	0.053	0.101	0.073
0.82	0.005	0.041	0.124	0.063
1.00	0.002	0.033	0.148	0.053
1.22	0.001	0.025	0.187	0.043
1.50	0.001	0.020	0.186	0.046
2.33	0.001	0.020	0.155	0.046
4.00	0.001	0.020	0.046	0.046

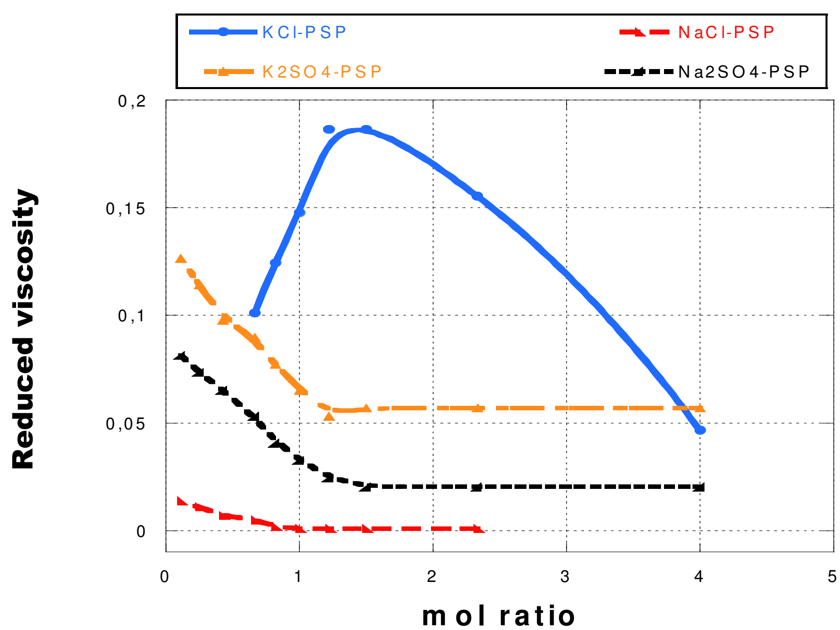


Figure 3. 8: $\eta_{rd} = f$(mol ratio) curves of $1x10^{-2}$ M various salt+$1x10^{-2}$ M PSP ($I=1x10^{-1}$M)

Viscosities values of $1x10^{-2}$ mol/L NaCl, PSP and NaCl + PSP mixtures in I=constant for different pH values were given in Table 3.11 and Figure 3.9.

Table 3. 11: Viscosity values in different pH for $1x10^{-2}$ mol/L NaCl, PSP and NaCl + PSP, ($I=1x10^{-1}$ M)

pH	reduced viscosity NaCl	reduced viscosity PSP	reduced viscosity NaCl-PSP
2	4.215	4.096	4.574
3	4.036	4.395	4.484
4	4.305	4.574	4.574
5	4.484	4.813	4.305
6	4.664	4.933	4.753
7	4.036	4.574	5.022
8	3.857	4.574	5.112

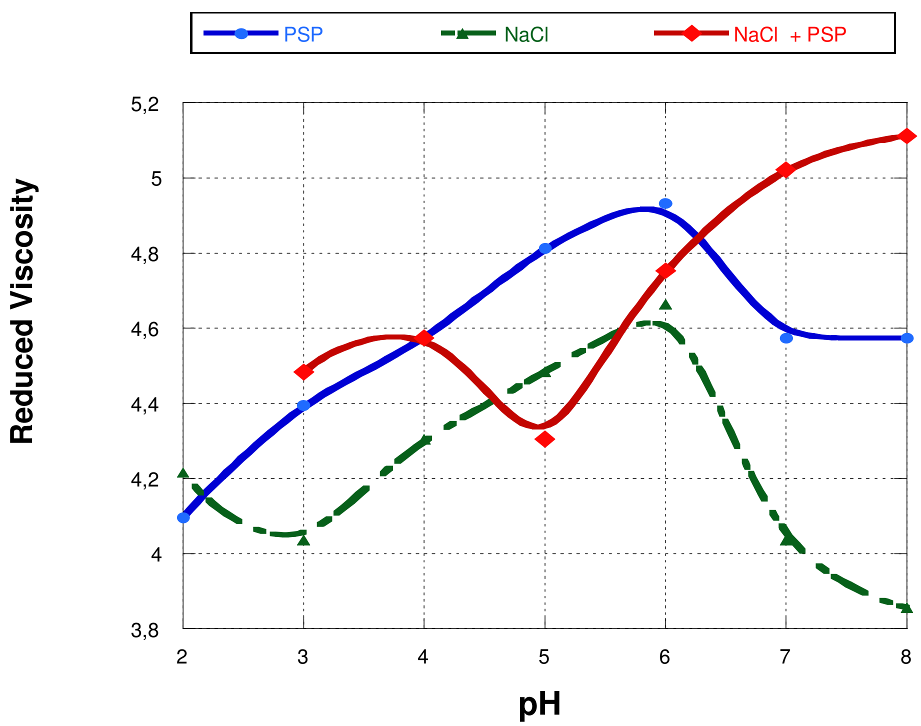


Figure 3. 9: $\eta_{rd} = f(\mathrm{pH})$ curves for $1x10^{-2}$mol/L NaCl ,PSP and NaCl +PSP ($I=1x10^{-1}$ M)

Viscosities of dilute solutions of $1x10^{-2}$ mol/L Na_2SO_4, PSP and Na_2SO_4 + PSP mixtures in I=constant for different pH values were given in Table 3.12 and Figure 3.10.

Table 3. 12: Viscosity values at different pH $1x10^{-2}$ mol/L Na_2SO_4 ,PSP and Na_2SO_4+ PSP,($I=1x10^{-1}$M)

pH	reduced viscosity Na_2SO_4	reduced viscosity PSP	reduced viscosity Na_2SO_4 -PSP
2	4.694	4.096	5.710
3	4.574	4.395	5.531
4	4.454	4.574	5.172
5	4.514	4.813	5.710
6	5.232	4.933	5.411
7	4.813	4.574	5.052
8	4.454	4.574	5.590

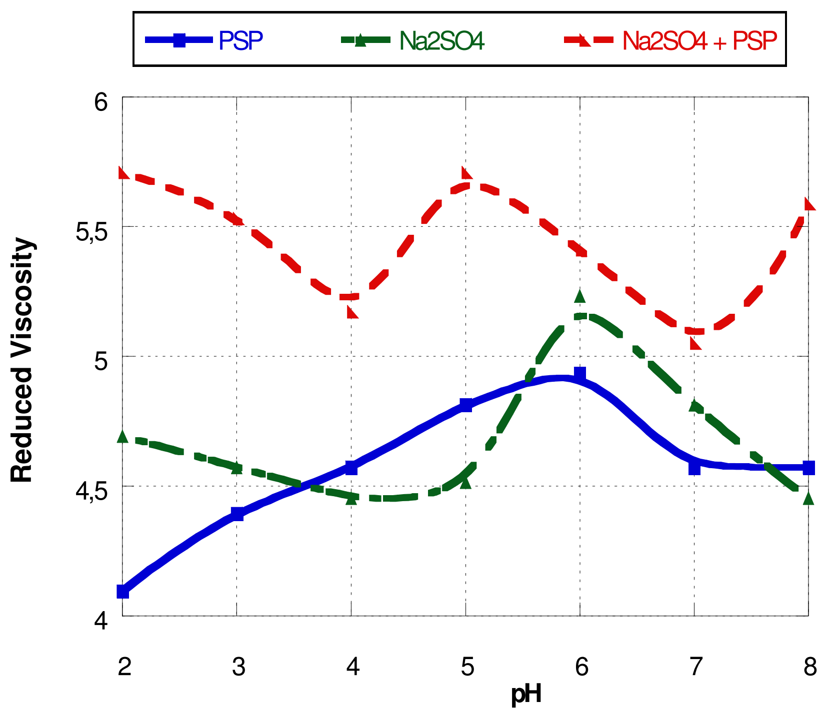


Figure 3. 10: $\eta_{rd} = f$(pH) Curves for $1x10^{-2}$ mol/L Na_2SO_4 , PSP and Na_2SO_4 +PSP, ($I=1x10^{-1}$ M)

Viscosities of dilute solutions of $1x10^{-2}$ mol/L KCl, PSP and KCl + PSP mixtures in I=constant for different pH values were given in Table 3.13 and Figure 3.11.

Table 3. 13: Viscosity values in different pH for $1x10^{-2}$ mol/L KCl, PSP and KCl + PSP ($I=1x10^{-1}M$)

pH	reduced viscosity KCl	reduced viscosity PSP	reduced viscosity KCl -PSP
2	4.664	4.096	4.694
3	4.454	4.395	4.873
4	4.215	4.574	4.634
5	4.126	4.813	4.275
6	4.036	4.933	4.156
7	3.946	4.574	3.976
8	4.036	4.574	4.873

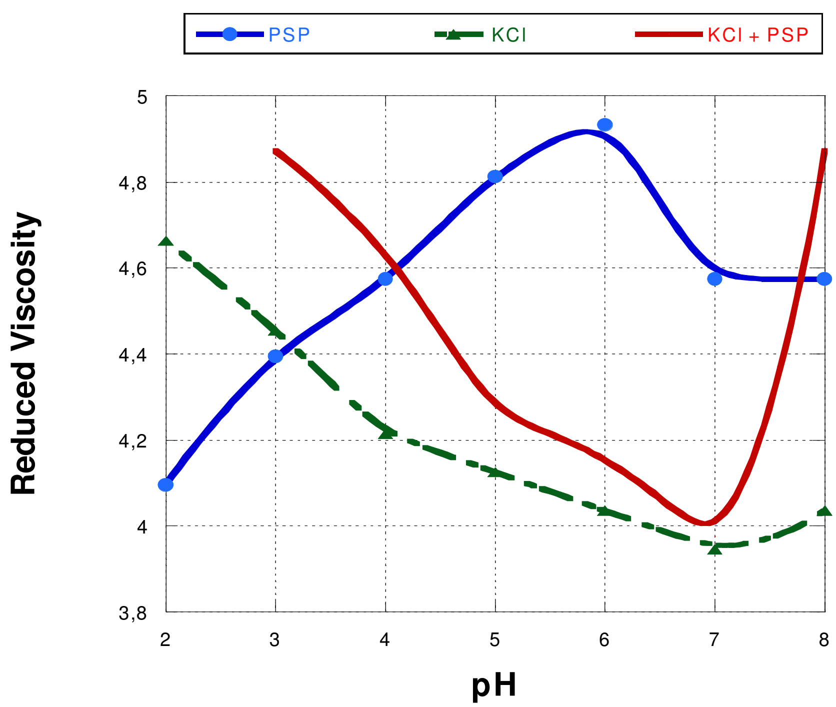


Figure 3. 11: $\eta_{rd} = f(\text{pH})$ Curves for $1x10^{-2}$ mol/L KCl , PSP and KCl + PSP, ($I=1x10^{-1}M$)

Viscosities of dilute solutions of $1x10^{-2}$ mol/L K_2SO, PSP and K_2SO_4 + PSP mixtures in I=constant for different pH values were given in Table 3.14 and Figure 3.12.

Table 3. 14: Viscosity values in different pH for $1x10^{-2}$ mol/L K_2SO_4, PSP and K_2SO_4 + PSP, ($I=1x10^{-1}M$)

pH	reduced viscosity K_2SO_4	reduced viscosity PSP	reduced viscosity K_2SO_4 - PSP
2	3.558	4.096	4.574
3	3.229	4.395	4.454
4	3.079	4.574	4.574
5	3.498	4.813	4.753
6	4.335	4.933	4.933
7	4.335	4.574	4.933
8	4.335	4.574	5.052

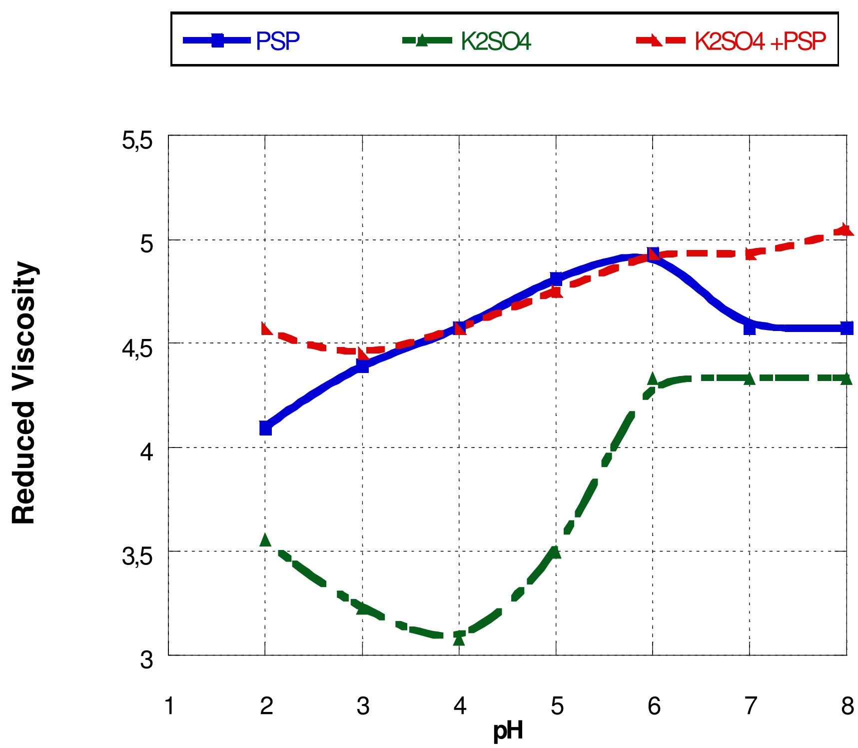


Figure 3. 12: $\eta_{rd} = f(pH)$ Curves for $1x10^{-2}$ mol/L K_2SO_4 , PSP and K_2SO_4 + PSP, ($I=1x10^{-1}M$)

3.5.4. Thermodynamic measurements

Equilibrium constants of microcations and microanions with poly(sodiumphosphate) as polyanion and poly(allylaminehydrochloride) as polycation for the optimum stoichiometry were determined by potentiometry as the function of temperature and pH parameters. In the case of diluted solution, this relationship is considered to be valid for salts (microions) both in the absence and presence of polycation and polyanion [25,26].

The experimental procedure is to measure pH of the microions in the presence and absence of PSP also PAH at different temperatures, and then the proton concentration is calculated corresponding to given expressions.

For weak acids the relation between the degree of dissociation (α), dissociation constant (Kα) and concentration C can be expressed as

$$K_\alpha = \left(\frac{[H^+][A^-]}{[HA]}\right) = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \qquad \textbf{(3.13)}$$

$$\alpha = \left(\frac{K_\alpha}{C}\right)^{1/2} \qquad \textbf{(3.14)}$$

Degree of dissociation can be approximated for weak acids (where 1-α =1)

$$\alpha = \frac{[H^+]}{C}$$

$[H^+] = (K\ \alpha\ X\ C\ )^{1/2}$

Finally degree of linkage (θ) is determined from the equation

$$\theta = \frac{(C_o - C)}{C_o} = 1 - \frac{C}{C_o} \qquad \textbf{(3.15)}$$

$$= 1 - \left(\frac{[H^+]}{[H^+]_o}\right)^2$$

$[H^+]_0$: the proton concentration in absence of PSP or PAH

$[H^+]$: The proton concentration in presence of PSP or PAH

C_0 : concentration of salt

C : concentration of salt + PSP or PAH

And then equilibrium constants of salt -polyion is calculated from the following equation

$$K= \frac{C_o \theta}{(C_o \ (1-\theta))^2} \quad \textbf{(3.16)}$$

Thermodynamic constants are calculated from the following equation.

$$\Delta G^o = - RT \ln K \quad \textbf{(3.17)}$$

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\ominus}{R} \quad \textbf{(3.18)}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\theta}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \textbf{(3.19)}$$

$$\Delta S = -\frac{(\Delta G^o - \Delta H^o)}{T} \quad \textbf{(3.20)}$$

The plots of pH, degree of linkage(θ), lnK, ΔG, ΔH and ΔS values for both I= varied and I=constant for PSP-salt solution and I= constant for PAH-salt solutions, as a function of temperature were obtained. The results for one PSP- NaCl solutions are given in Table 3.15, Figure 3.13 – 3.18

Table 3. 15: Equilibrium constant of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

t oC	PSP+NaCl pH	NaCl pH	H+	H_o+	$(H+/H_o^+)^2$	θ *	K	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
20	6.42	6.61	3.802E-07	4.169E-07	8.32E-01	1.68E-01	2.43E+03	7.80	-18.99	1.75	88.14
25	6.27	6.12	5.370E-07	7.586E-07	5.01E-01	4.99E-01	1.99E+04	9.90	-24.52	1.82	100.43
30	6.00	5.73	1.000E-06	1.862E-06	2.88E-01	7.12E-01	8.56E+04	11.36	-28.61	-0.59	89.69
35	5.84	5.60	1.445E-06	2.512E-06	3.31E-01	6.69E-01	6.10E+04	11.02	-28.22	-3.28	69.42
40	5.05	4.92	8.913E-06	1.202E-05	5.50E-01	4.50E-01	1.49E+04	9.61	-25.01	2.43	94.27
45	6.12	5.93	7.586E-07	1.175E-06	4.17E-01	5.83E-01	3.36E+04	10.42	-27.55	3.50	105.26
50	5.92	5.65	1.202E-06	2.239E-06	2.88E-01	7.12E-01	8.56E+04	11.36	-30.50	4.85	118.02
55	3.33	2.96	4.677E-04	1.096E-03	1.82E-01	8.18E-01	2.47E+05	12.42	-33.86	7.09	135.29
60	4.70	4.20	1.995E-05	6.310E-05	1.00E-01	9.00E-01	9.00E+05	13.71	-18.99	1.75	88.14

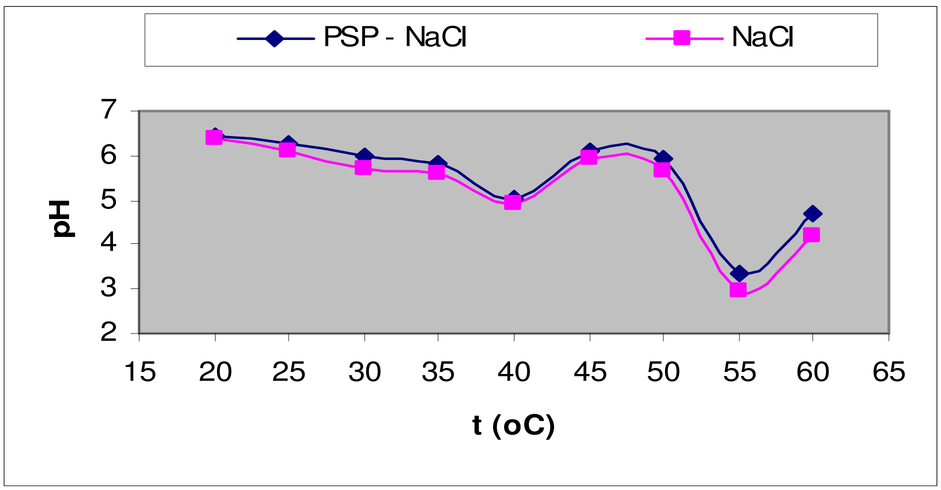


Figure 3. 13: pH=f (t°C) curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

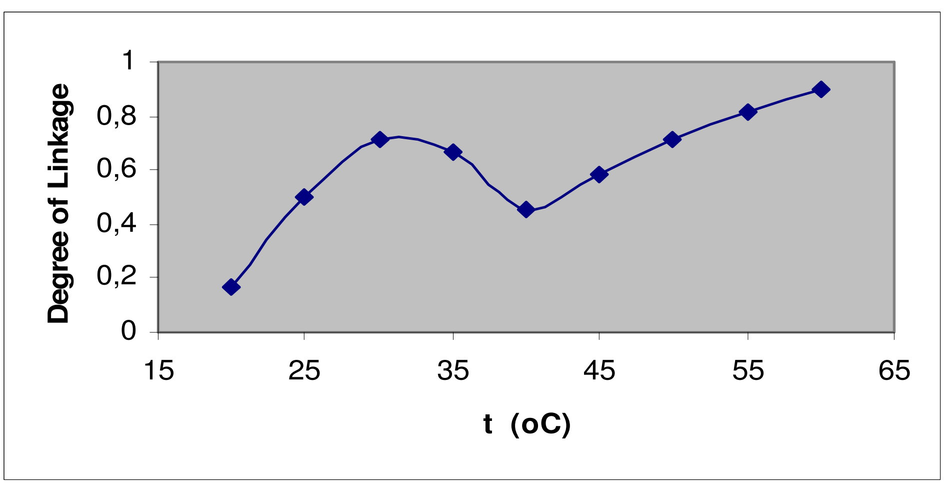


Figure 3. 14: Degree of Linkage, θ =f (t°C) Curve of $1x10^{-4}$(mo/L) PSP- $1x10^{-4}$(mo/L) NaCl

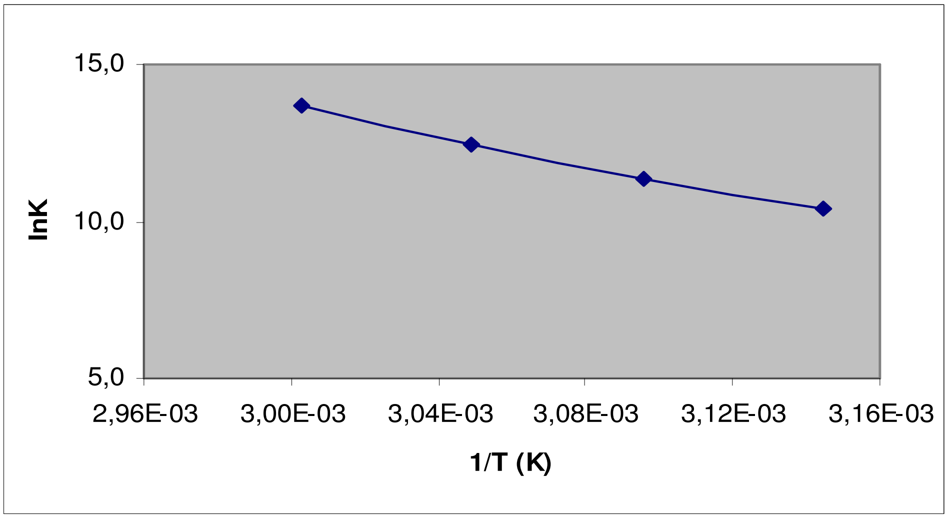


Figure 3. 15: lnK= f (1/T) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$ (mo/L) NaCl

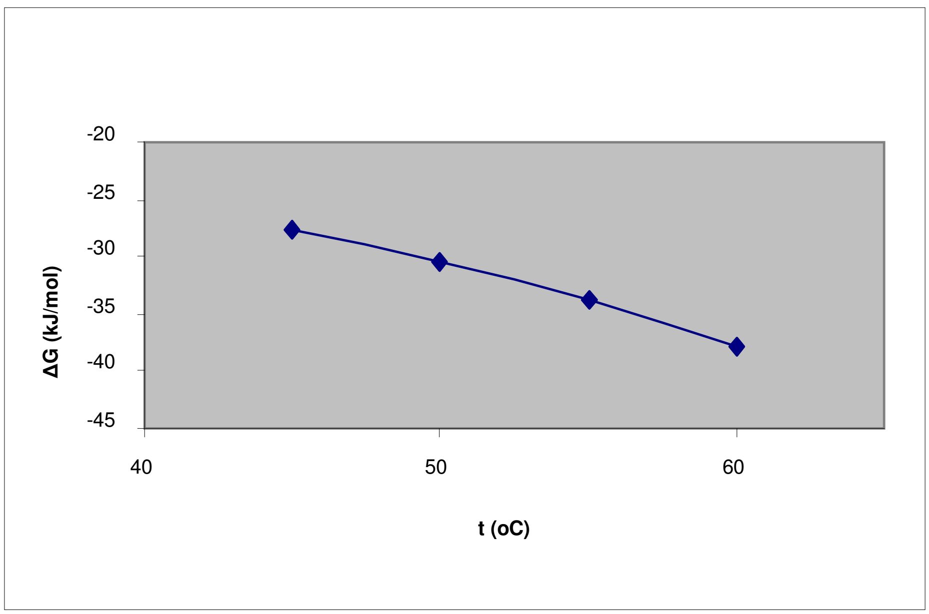


Figure 3. 16: ΔG=f (t°C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

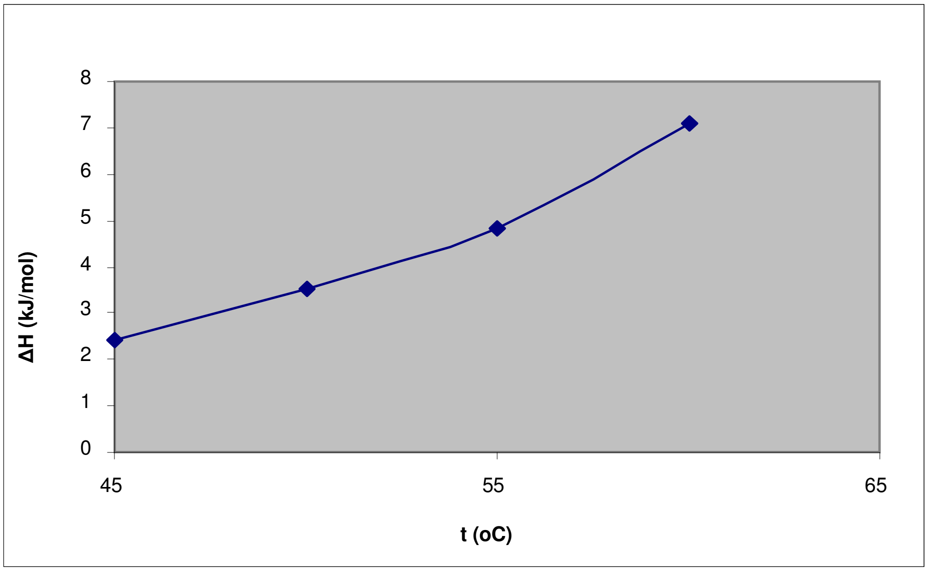


Figure 3. 17: ΔH= f (t °C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

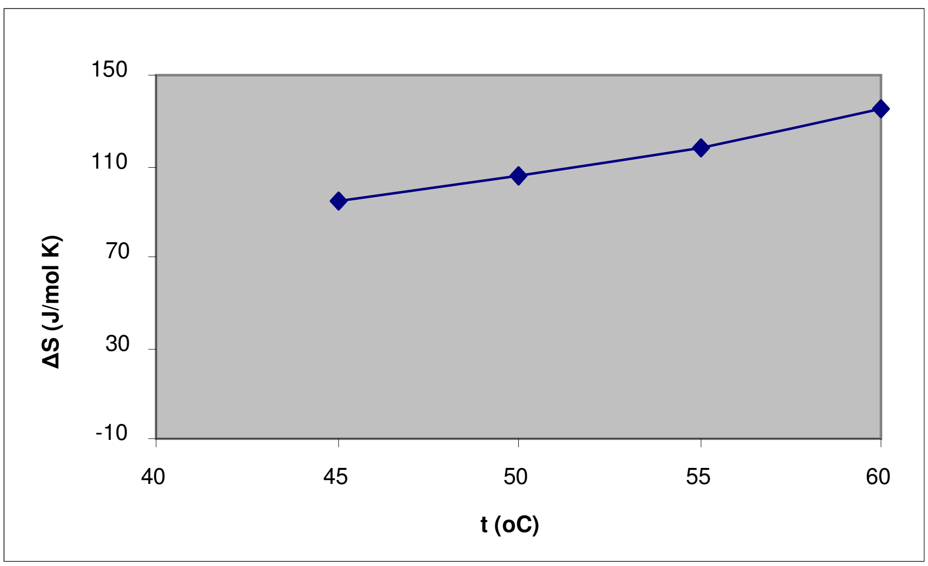


Figure 3. 18: ΔS= f (t °C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

The rest of the results for polyion- salts are given in table. 3.16 and Appendix E, and Figures in Appendix B, C,and D.

Table 3. 16: Thermodynamic values for PSP – NaCl solution (I= varied)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-1}$M PSP-NaCl	20	0.87	6.31	-15.38		
	25	0.89	6.51	-16.13	0.16	54.67
	30	0.91	7.09	-17.87	0.73	61.37
	35	0.84	5.81	-14.89	-2.23	41.09
	40	0.48	2.85	-7.41	-6.90	1.62
	45	0.74	4.67	-12.34	5.45	55.95
	50	0.84	5.81	-15.61	4.29	61.61
	55	0.91	7.00	-19.08	5.41	74.65
	60	0.95	8.43	-23.33	7.85	93.63
$1x10^{-2}$M PSP-NaCl	20	0.92	9.49	-23.12		
	25	0.96	11.01	-27.28	1.26	95.79
	30	0.70	6.64	-16.73	-5.45	37.22
	35	0.99	12.97	-33.22	11.05	143.73
	40	0.89	8.81	-22.93	-9.68	42.33
	45	0.80	7.61	-20.11	-3.61	51.89
	50	0.54	5.56	-14.93	-7.66	22.53
	55	0.89	8.91	-24.30	15.32	120.78
	60	0.95	10.63	-29.44	9.47	116.84
	t^oc	**θ**	**lnK**	**ΔG(kJ/mol)**	**ΔH(kJ/mol)**	**ΔS(J/mol^{o}K)**
$1x10^{-3}$M PSP-NaCl	20	0.68	8.83	-21.51		
	25	0.81	10.01	-24.81	0.98	86.54
	30	0.67	8.72	-21.96	-1.62	67.13
	35	0.96	13.22	-33.85	7.86	135.45
	40	0.90	11.31	-29.43	-4.45	79.83
	45	0.60	8.24	-21.79	-9.18	39.65
	50	0.21	5.79	-15.54	-9.19	19.67
	55	0.60	8.24	-22.48	11.23	102.76
	60	0.83	10.32	-28.57	11.39	120.00
$1x10^{-4}$M PSP-NaCl	20	0.17	7.80	-18.99	1.75	88.14
	25	0.50	9.90	-24.52	1.82	100.43
	30	0.71	11.36	-28.61	-0.59	89.69
	35	0.67	11.02	-28.22	-3.28	69.42
	40	0.45	9.61	-25.01	2.43	94.27
	45	0.58	10.42	-27.55	3.50	105.26
	50	0.71	11.36	-30.50	4.85	118.02
	55	0.82	12.42	-33.86	7.09	135.29
	60	0.90	13.71	-18.99	1.75	88.14

3.5.5 IR spectrum

IR spectra of PSP, PSP+NaCl and PSP+Na_2SO_4 (I=Constant) are given in the following.

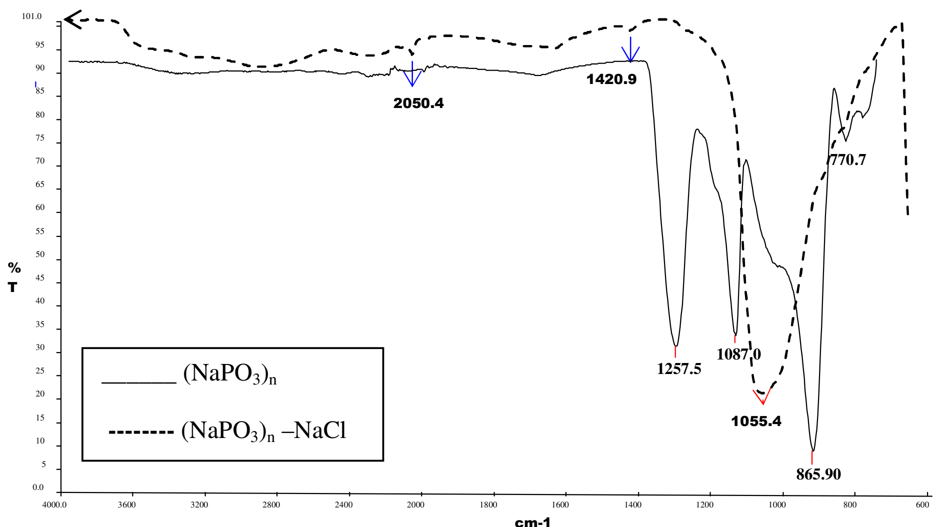


Figure.3.19 : IR spectrum $1x10^{-2}$ (mol/L) PSP +$1x10^{-2}$ (mol/L) NaCl, (I=$1x10^{-1}$ mol/L)

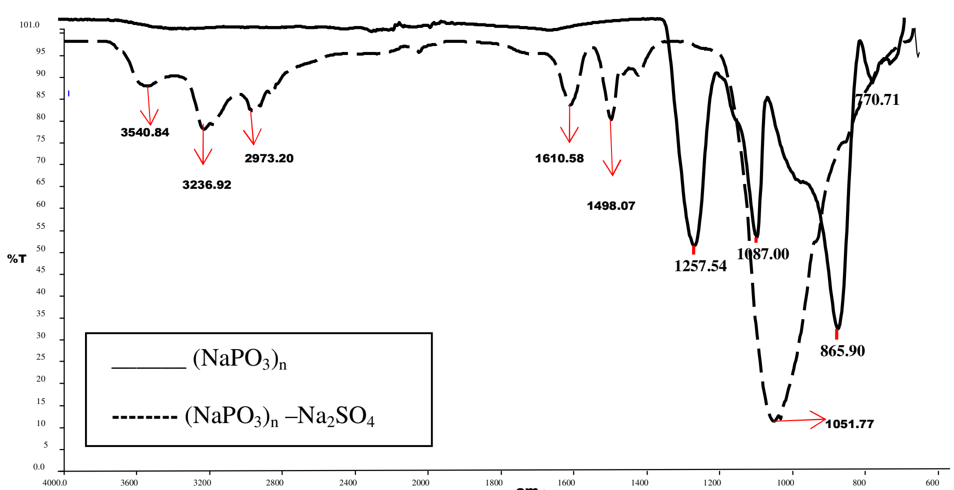


Figure 3. 20: IR spectrum $1x10^{-2}$ (mol/L) PSP + $1x10^{-2}$ (mol/L) Na_2SO_4, (I=$1x10^{-1}$ mol/L)

The rest of the IR spectra of PSP, PAH, PSP+ various salt, PAH+various salt (I=constant, and I=varied) are given in the Appendix F.

4. RESULTS AND DISCUSSION

An accurate description of the stoichiometry and mode of counter ion binding to the polyion has been a central goal of the experimental and theoretical study of polyelectrolyte solution.

The definition of counter(=coion) binding to polyelectrolyte depending on the experimental studies can often be given as the close approach of coion and polyion with the mutual perturbation of hydrated layers [3]. Counter ions from a state of free hydration into an environment of perturbed hydration are called to pass from a free to bound state. Record et all., have introduced the definition of "thermodynamic binding" which includes ionic atmospheric, or screening effects. Their definition has proved useful in thermodynamic calculations. In this interaction the resulting volume changes, can mainly be measured by volumetric methods. Conductometry is one of the most satisfactory methods to study polyelectrolyte and low molecular weight salts interactions in aqueous solution.

The result of conductometric titration showed that the interaction between polyanion (PSP)/polycation (PAH) and various low molecular weight salts, in general, did not varied significantly depending on the polyions and microions concentrations, ionic strength, counter ion type and pH, and almost the same kind of titration curve was obtained. The mole ratio of polyion to low molecular weight salts (coions) was found to be nearly stoichiometric (Table 3.4, 3.5, 3,6, 3.7, Appendix A FiguresA.1-A.75), but the charge ratio deviated to a degree from 1:1 ratio of polyion to microion (Table 3.8, Appendix A Figures A.75 – A.84).

The increase in the conductometric titration curves reveals that conductivity originates from the ionization of polyion and microions, and then the curve remain constant due to charge condensation on/domain of polyion. The charge condensation equilibrium can be provided by territorial binding and a small fraction of site binding

A few curves in different mode was obtained for $1x10^{-2}$ mol/L, $1x10^{-4}$mol/L NaCl and Na_2SO_4 interaction with polyanion, PSP,(Appendix Figure A.21,A.23 and A.27), also $1x10^{-3}$mol/L KCl and K_2SO_4, $1x10^{-4}$mol/L Na_2SO_4 interaction with polycation, PAH,(Appendix A Figure A.64, A.66 and A.69) in ionic strength, I=varied and I=constant solution. The decrease part of the curve indicate that the interaction occurs from the beginning of titration, and after reaching 1:1 ratio, curve becomes constant. The interaction of $1x10^{-2}$ mol/L Na_2SO_4 with PAH (Appendix, Figure A.62) and $1x10^{-3}$ mol/L KCl with PSP (Appendix,Figure A.29) results in the titration curve with a continuous line from the beginning of the titration.

The various salt chosen in the experiments was aimed to see the effects of different micro cations and anions on the interaction with polyions, but the results revealed that there is no distinct differences in their effects on polyions except potassium ion (Figure 3.8). This exceptional case of potassium ion arises because of its free state is slightly hydrated(small hydration radius) so that its territorial binding will be significantly weak. This means that overlapping of coulomb fields of the charged groups in the territory of polyion will not predominate.

The pH effect on the interaction of polyions and microions as shown in Figures 3.5 and 3.6 exhibit the same mode. The separate part indicating the interaction between PSP and KCl and NaCl originates from pH=3 value which corresponds the pK value of poly acids form of poly(sodiumphosphate).

Charge dansities decreases by the addition of microions, thus the average separation of polyions from each other become larger, and individual coiling of the polyions occur. Coiling via intramolecular hydrogen bond may be predicted from the variations of viscosity values.

The result of viscosity studies are given by the curves of $\eta_{sp} = f$(pH) (Figure 3.10 - 3.13) and $\eta_{sp} = f$(mol ratio) (Figure 3.8). The decrease and increase part of viscosity curves reveals the interaction and ionization phenomena respectively and constant part of curves indicate the condensation of microions on/domain polyions. As shown in the viscosity curves, experimental parameters related with the polyion/salt ratio which is about 1:1 confirmed the conductometric results. In the Na_2SO_4, K_2SO_4 and KCl salts cases a slight deviations from the unity was observed.

The thermodynamic characteristics of polyions and microions interaction such as changes in equilibrium constants, Gibbs free energy, enthalpy and entropy was estimated from pH measurements as a function of temperature. From the pH measurements for the H-bonded complex system at a given temperature "Degree of linkage, θ", which is the ratio of interacting counterions upon polyions were determined, thus equilibrium constant and thermodynamic above given state functions associated with interaction reaction were calculated.

The magnitude of the thermodynamic data may give the "degree of screening" in the coulomb interaction system. The results of thermodynamic data of the interaction between polyions and microions in I=varied and I=constant solution are given in table 3.16- 3.17 and figures in Appendix B,C, D, E.

As a consequence, negative ΔG values for the given temperature indicates that the interaction proceeds readily without screening effect of counterions. Also, the increasing value of ΔH and ΔS in the given temperatures reveals that counter ions do not perform screening effect. The decreasing values of ΔH and ΔS in the certain range of temperatures indicates that a significant screening effect of counter ion occurs(Appendix B,C,D).

The curves of degree of linkage = $f(t\ ^{o}c)$ for all types of salts showed different mode depending on the temperature, and different increasing and decreasing values were obtained in the different temperature range. These variations suggested that the fraction of bound or un-bound counter ions can be correlated with the hydrated radius of cations. The fraction of bound counter ions decreases with the decreasing hydrated radius of cations. On the contrary, increment in the binding strength reveals the large hydration radius of cations.

The result of lnK values for all the interacted systems varied depending on the different temperature range. This results showed that the binding strength of the systems can be concluded for every different temperature range which can be determined to the application purposes.

5. CONCLUSION

In the present study, the equilibrium is achieved by columbic interaction predominantly. Polyion is in an extended conformation in the aqueous solution due to the high dielectiric constant of H_2O.

The temperature dependence of thermodynamic data bears in mind that Bjerrum distance in a coulombic system must be considered because of its magnitude is comparable with coulomb distance. If the Bjerrum distance is larger than coulomb distance, charge condensation takes place on the polyions, thus territorial binding occurs predominantly.

During the addition of low molecular weight salts to polyion, the coulombic entanglement at the domain of the interacted site of the polyion and coions (ions of LMWS) occurs due to the total charges of the polyion chains, and from the substantial ionization of counter ions. Counter ions suppress the interaction between polyions and enters between the polyions causing screening effect, thus the interaction of free polyions are slown down. As a result, polyion have a coiled conformation to bring its active site to react with the ions of LMW salts.

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APPENDICES

APPENDIX A: Figures For Conductometrik Titrations

APPENDİX B: Figures of Thermodynamic Results for PSP-Salt I=Varied

APPENDİX C: Figures of Thermodynamic Results for PSP-Salt I=Constant

APPENDIX D: Figures of Thermodynamic Results for PAH-Salt I=constant

APPENDIX E: Table of Thermodynamic Values

APPENDIX F: IR Spectrums of PSP, PAH, PSP-Salt, and PAH-salt

APPENDIX A: Figures For Conductometric Titrations

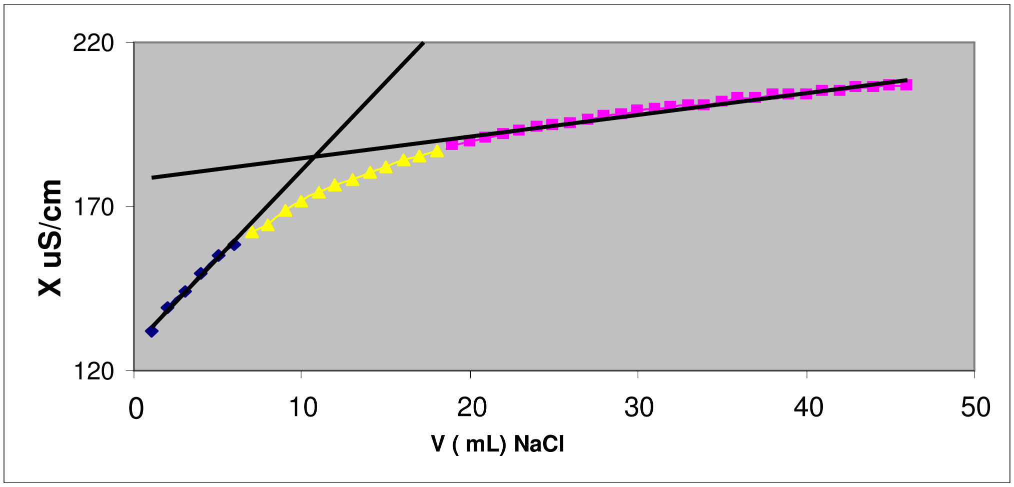

Figure A.1 : Titration $1x10^{-1}$ mol/L PSP with $1x10^{-1}$mol/L NaCl

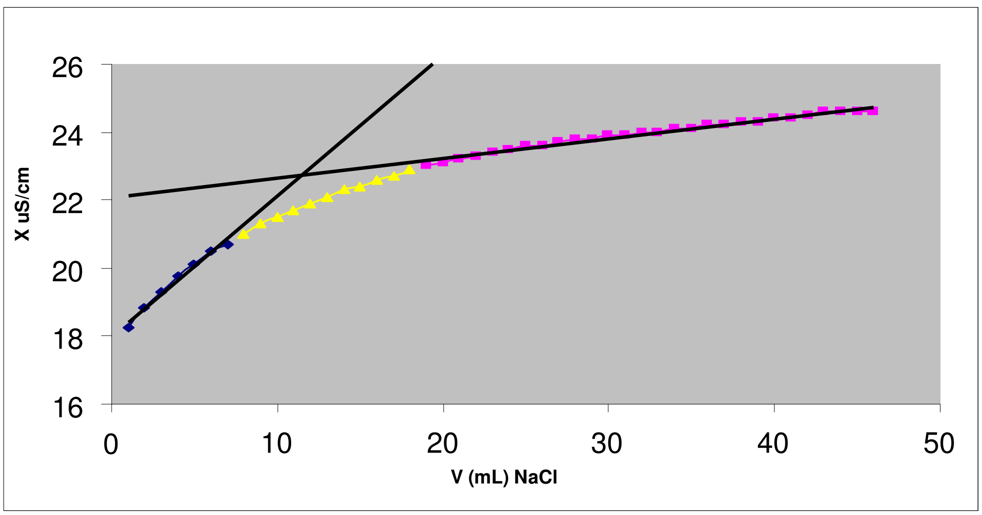

Figure A.2 : Titration $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L NaCl

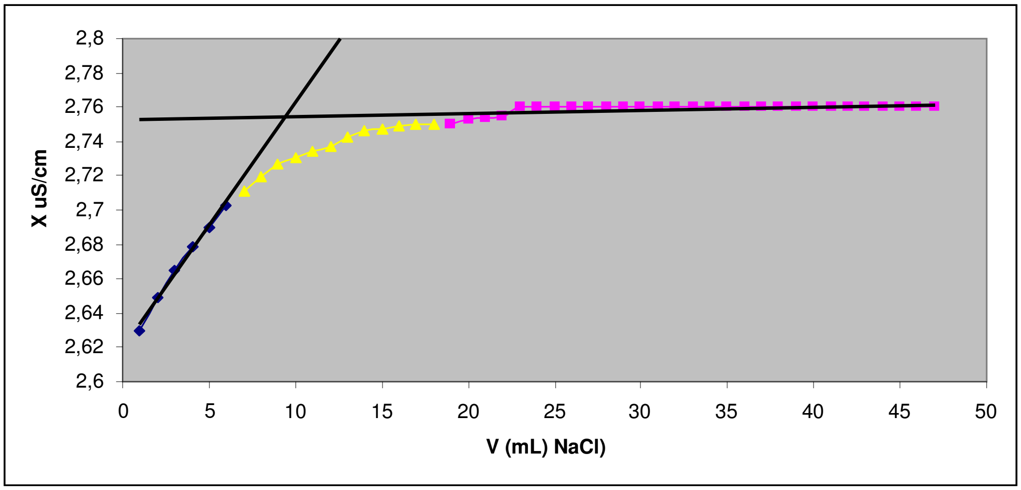

Figure A.3 : Titration $1x10^{-3}$ mol/L PSP with $1x10^{-3}$ mol/L NaCl

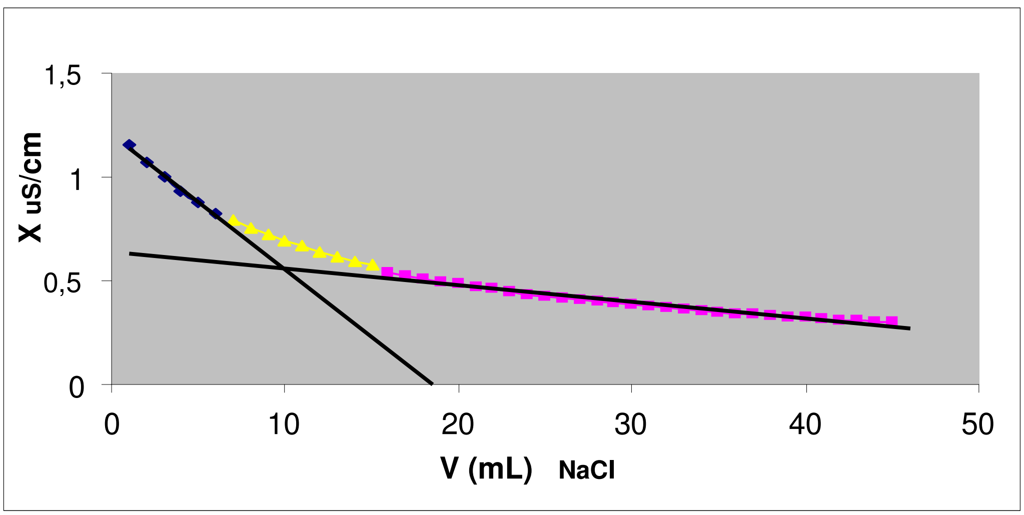

Figure A.4 : Titration $1x10^{-4}$ mol/L PSP with $1x10^{-4}$ mol/L NaCl

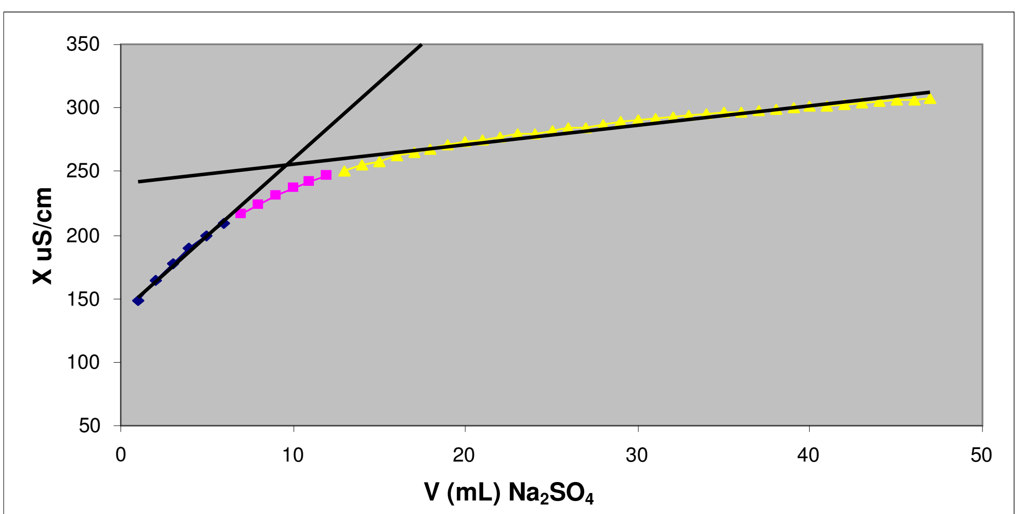

Figure A.5 : Titration $1x10^{-1}$ mol/L PSP with $1x10^{-1}$ mol/L Na_2SO_4

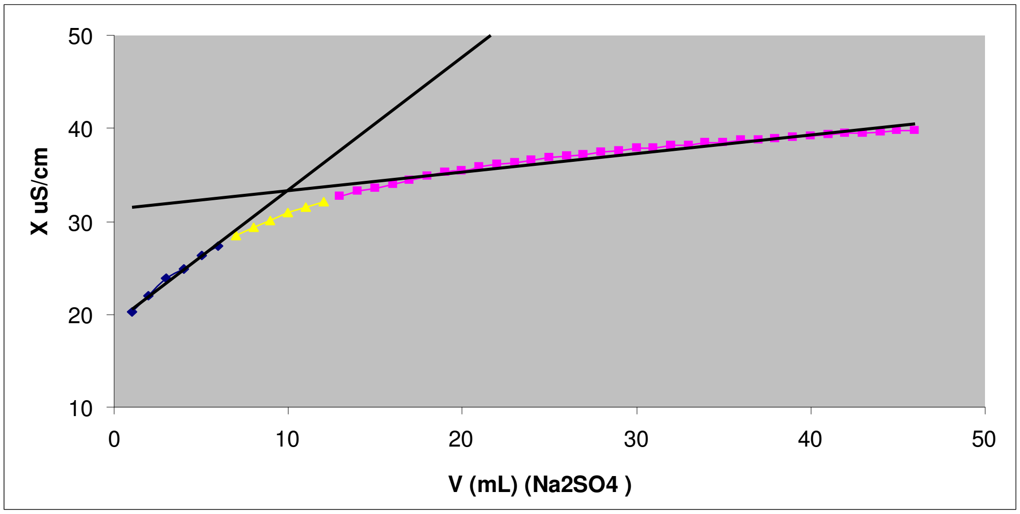

Figure A.6 : Titration $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L Na_2SO_4

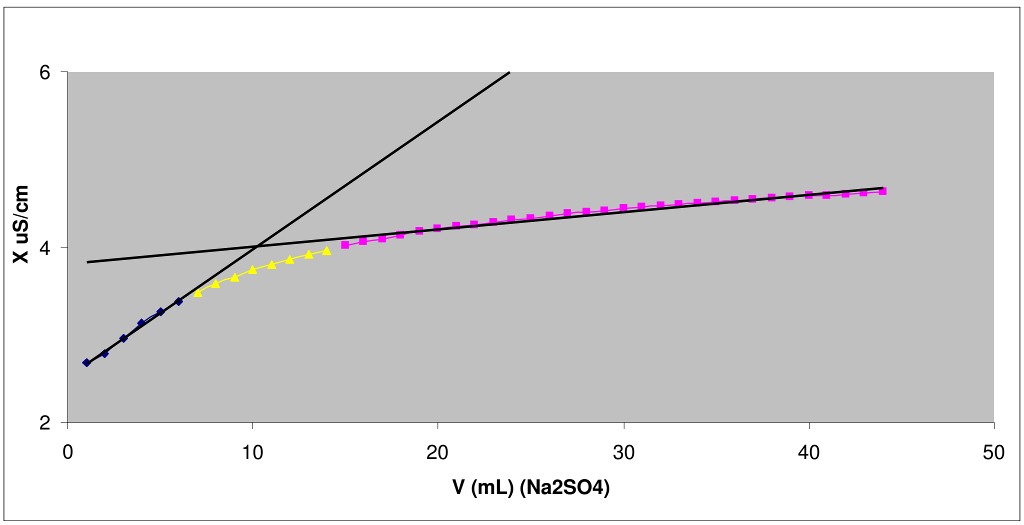

Figure A.7 : Titration $1x10^{-3}$ mol/L PSP with $1x10^{-3}$ mol/L Na_2SO_4

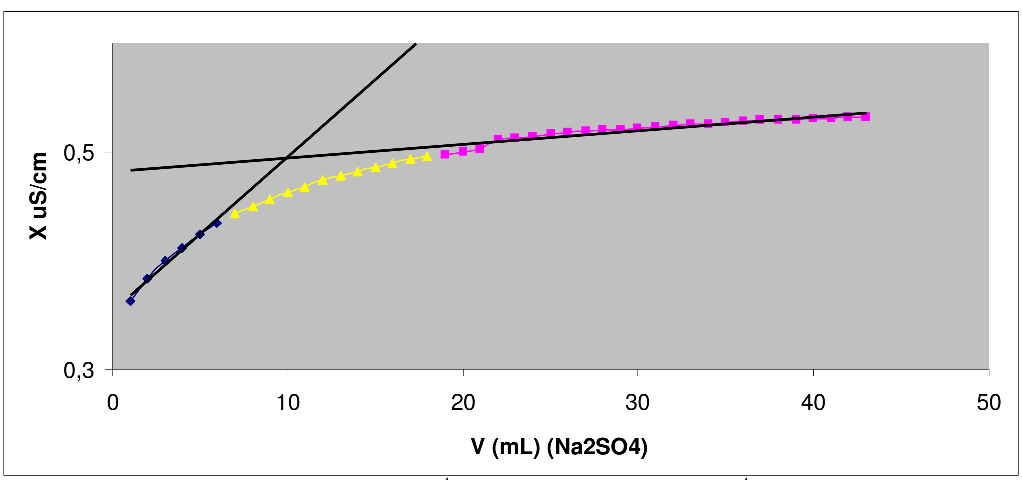

Figure A.8 : Titration $1x10^{-4}$ mol/L PSP with $1x10^{-4}$ mol/L Na_2SO_4

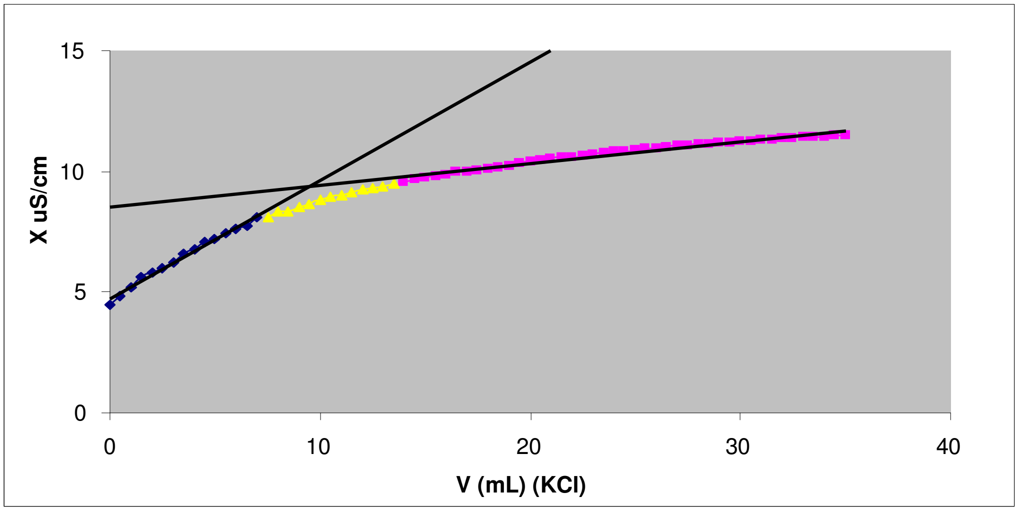

Figure A.9 : Titration $1x10^{-1}$ mol/L PSP with $1x10^{-1}$ mol/L KCl

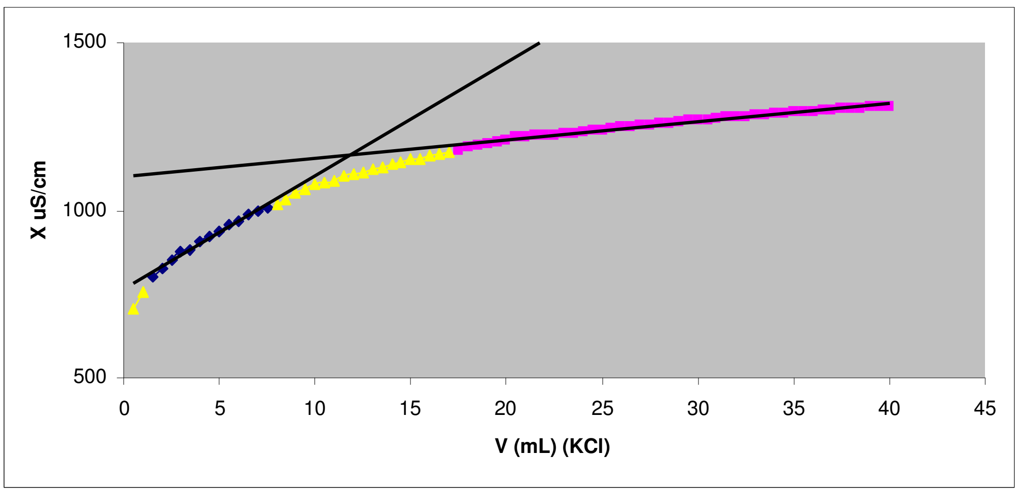

Figure A.10 : Titration curve $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L KCl

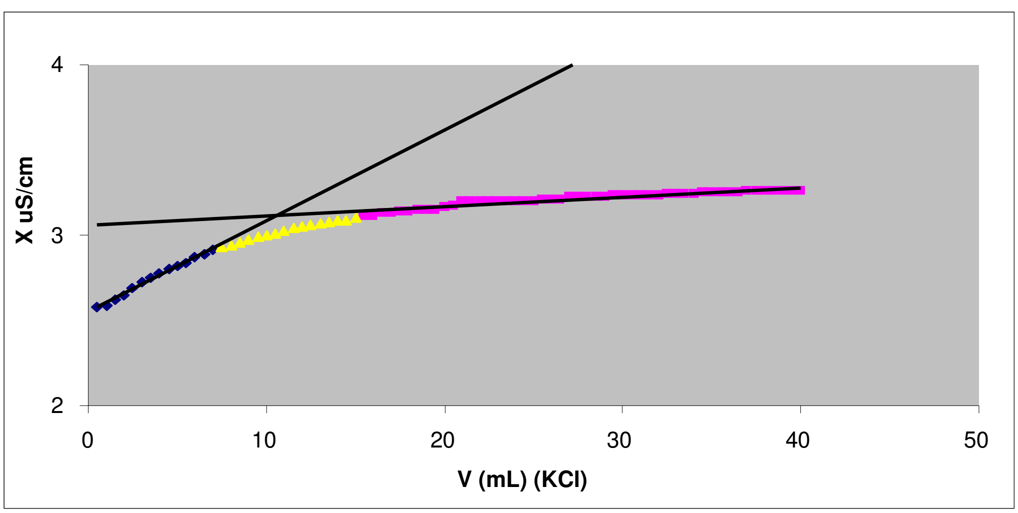

Figure A.11 : Titration $1x10^{-3}$ mol/L PSP with $1x10^{-3}$ mol/L KCl

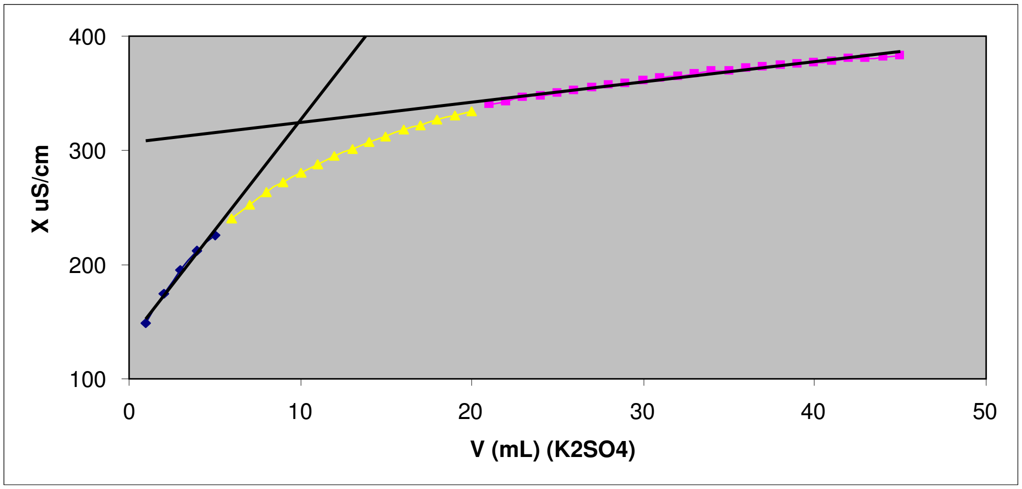

Figure A.12 : Titration $1x10^{-1}$ mol/L PSP with $1x10^{-1}$ mol/L K_2SO_4

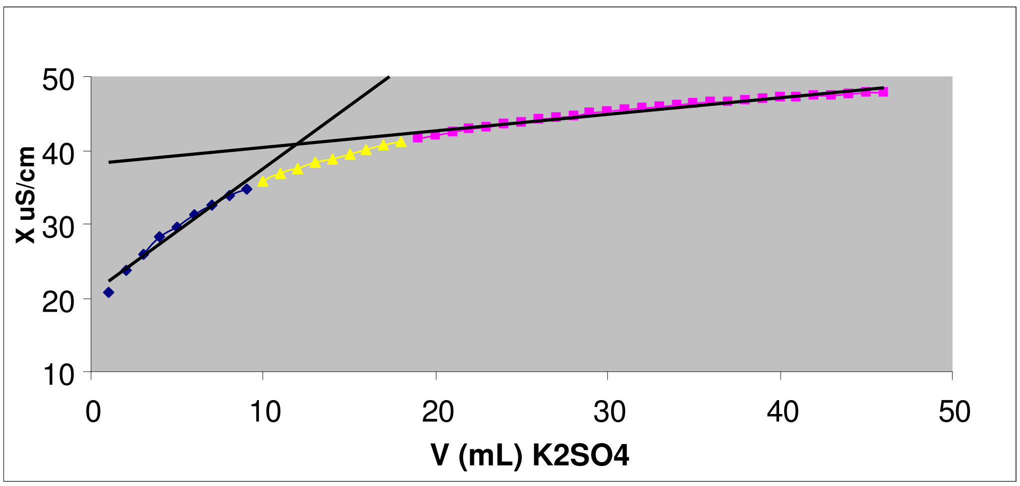

Figure A.13 : Titration $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L K_2SO_4

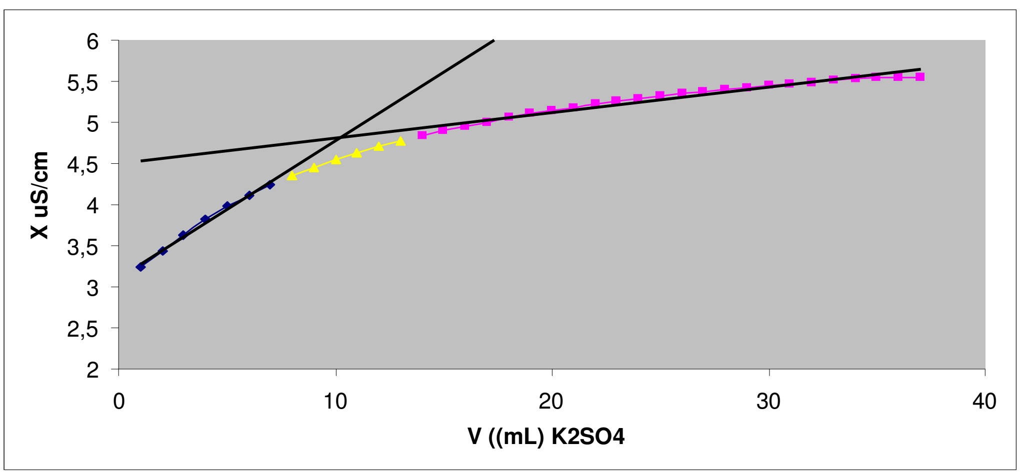

Figure A.14 : Titration $1x10^{-3}$ mol/L PSP with $1x10^{-3}$ mol/L K_2SO_4

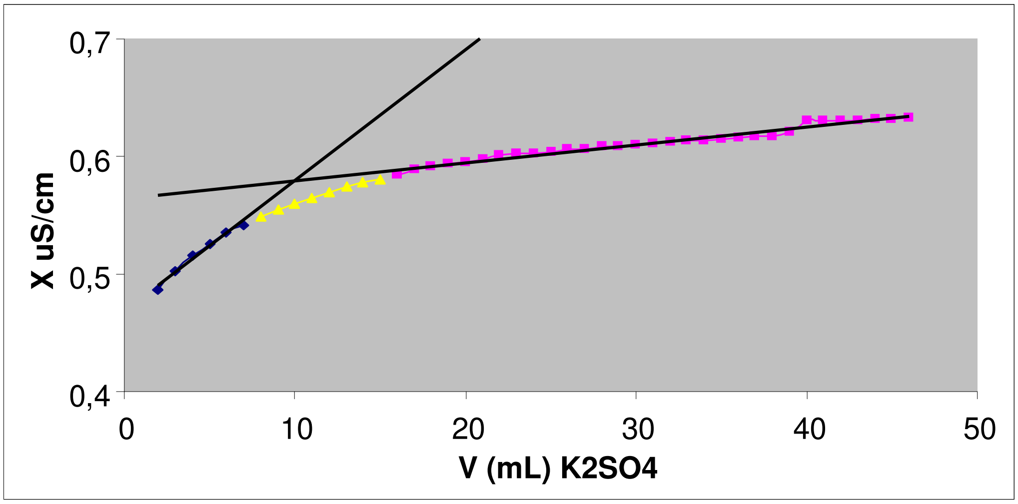

Figure A.15 : Titration $1x10^{-4}$ mol/L PSP with $1x10^{-4}$ mol/L K_2SO_4

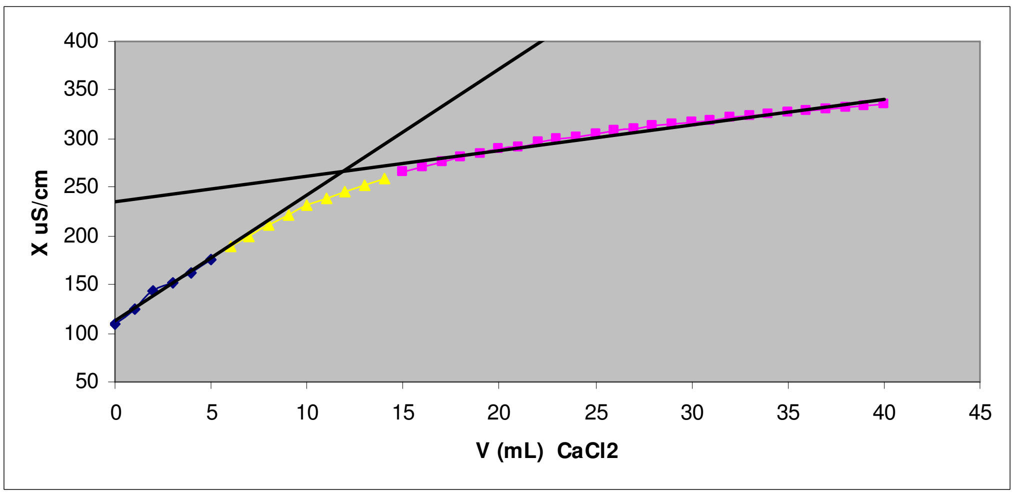

Figure A.16 : Titration $1x10^{-1}$ mol/L PSP with $1x10^{-1}$ mol/L $CaCl_2$

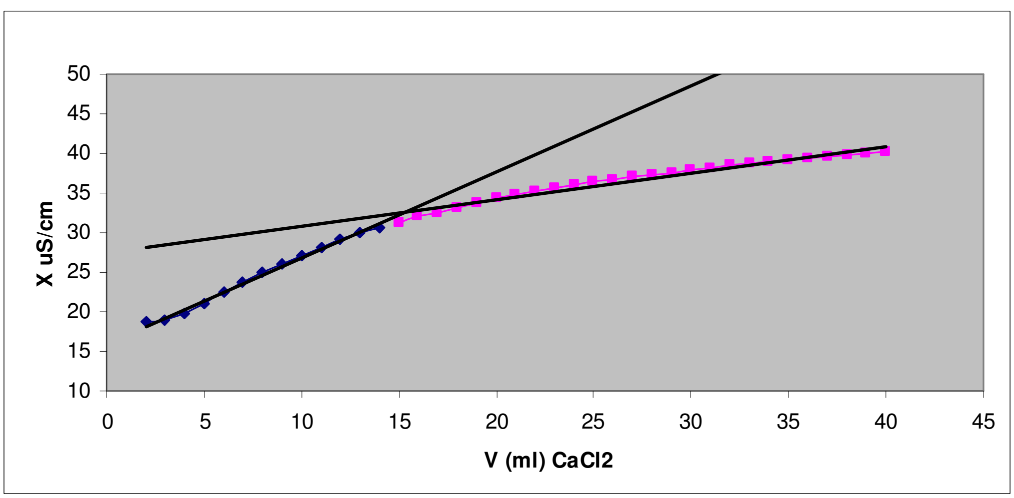

Figure A.17 : Titration $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L $CaCl_2$

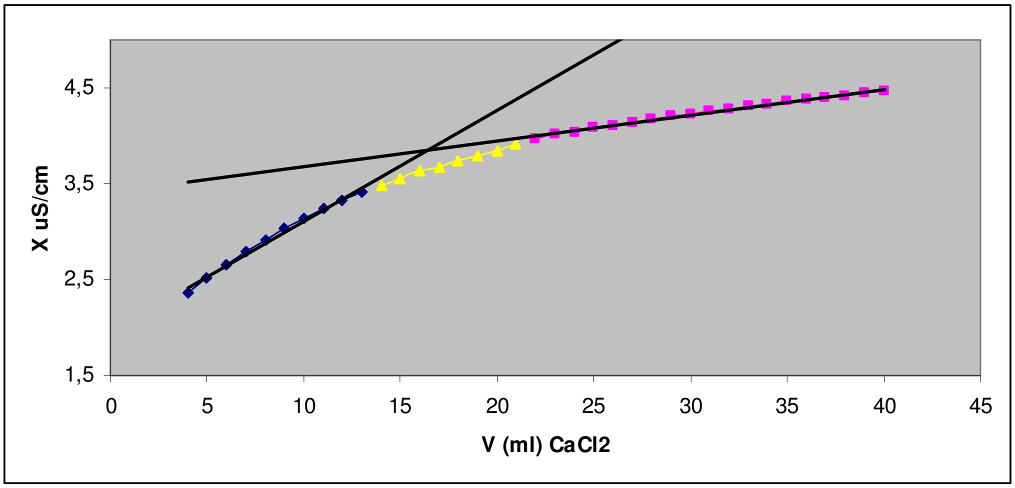

Figure A.18 : Titration 1x10^{-3} mol/L PSP with 1x10^{-3} mol/L $CaCl_2$

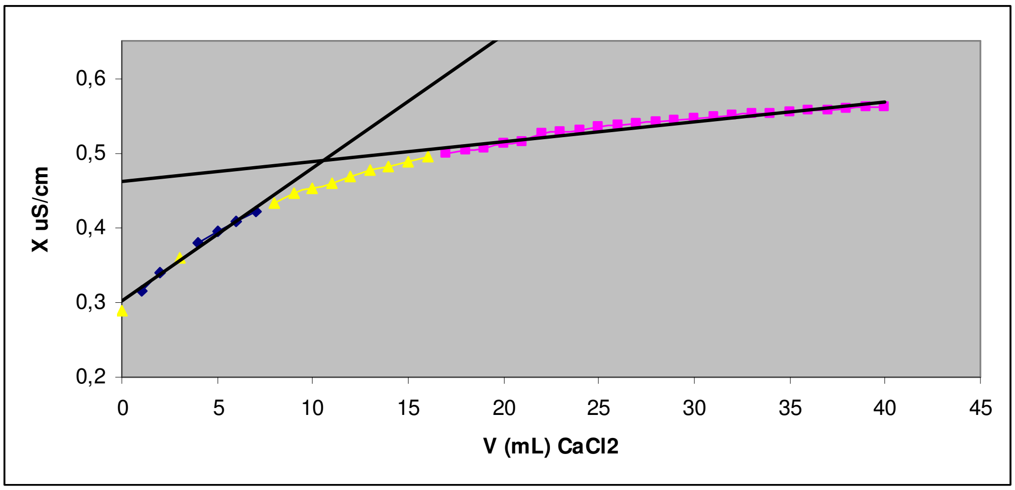

Figure A.19 : Titration 1x10^{-4} mol/L PSP with 1x10^{-4} mol/L $CaCl_2$

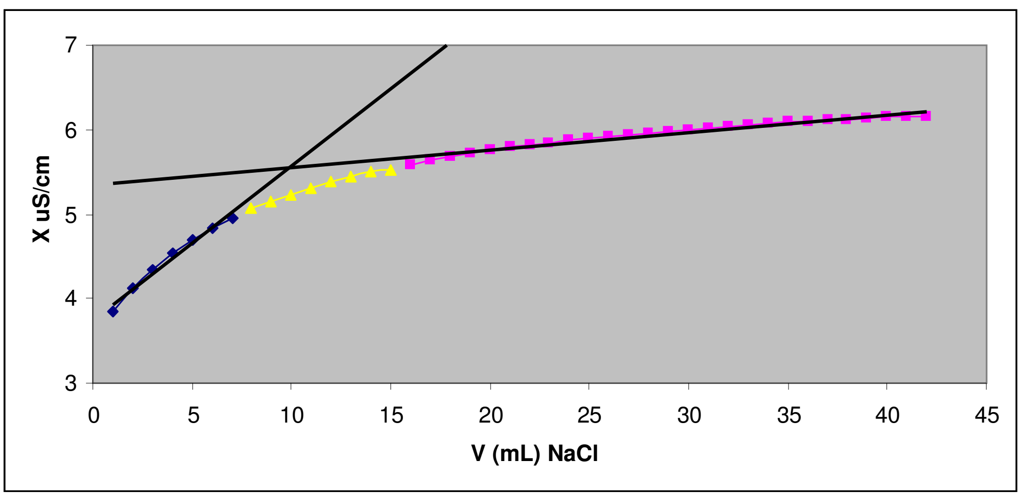

Figure A.20 : Titration 1x10^{-1} mol/L PSP with 1x10^{-1} mol/L NaCl (I=1mol/L)

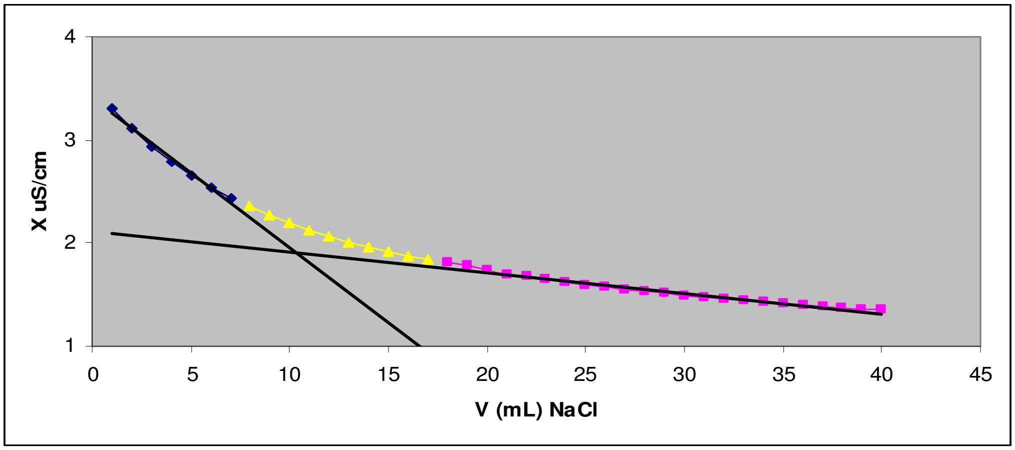

Figure A.21 : Titration $1x10^{-2}$ mol/L PSP with $1x10^{-2}$ mol/L NaCl, ($I=1x10^{-1}$ mol/L)

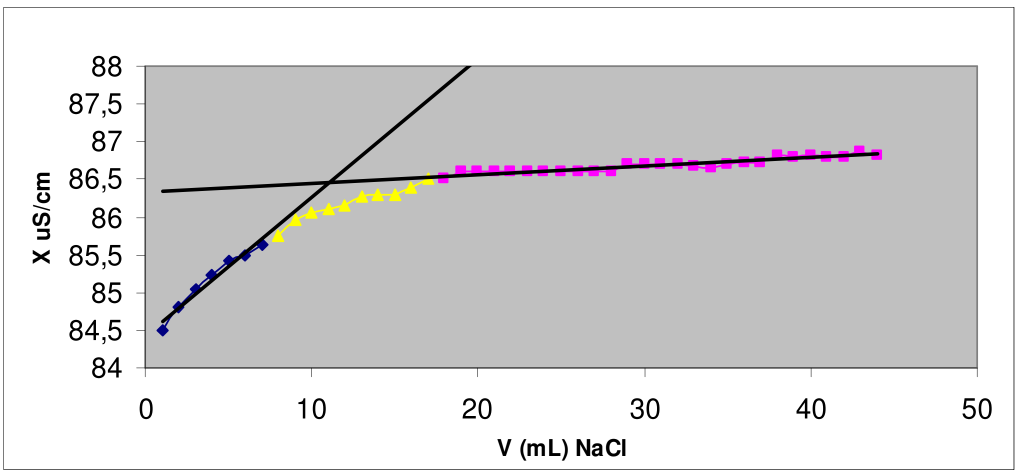

Figure A.22 : Titration $1x10^{-3}$ mol/L PSP with $1x10^{-3}$ mol/L NaCl, ($I=1x10^{-2}$ mol/L)

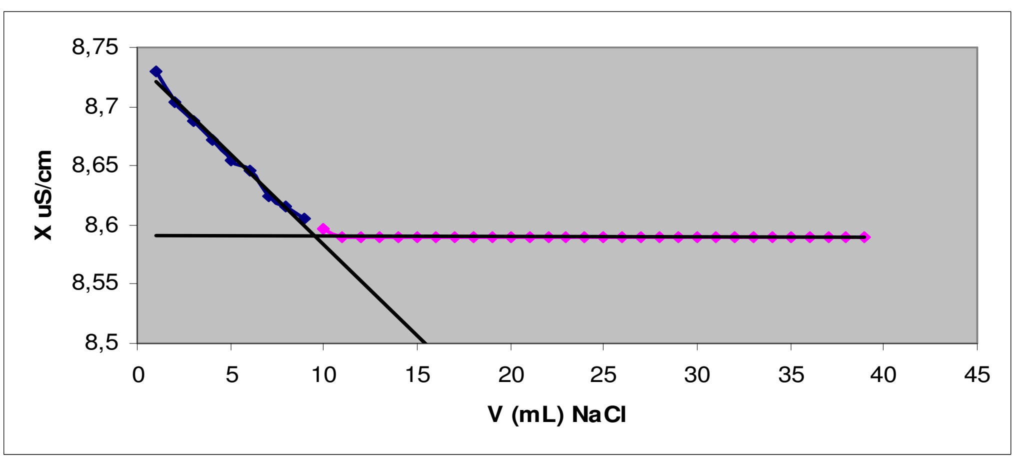

Figure A.23 : Titration $1x10^{-4}$ mol/L PSP with $1x10^{-4}$ mol/L NaCl, ($I=1x10^{-3}$ mol/L)

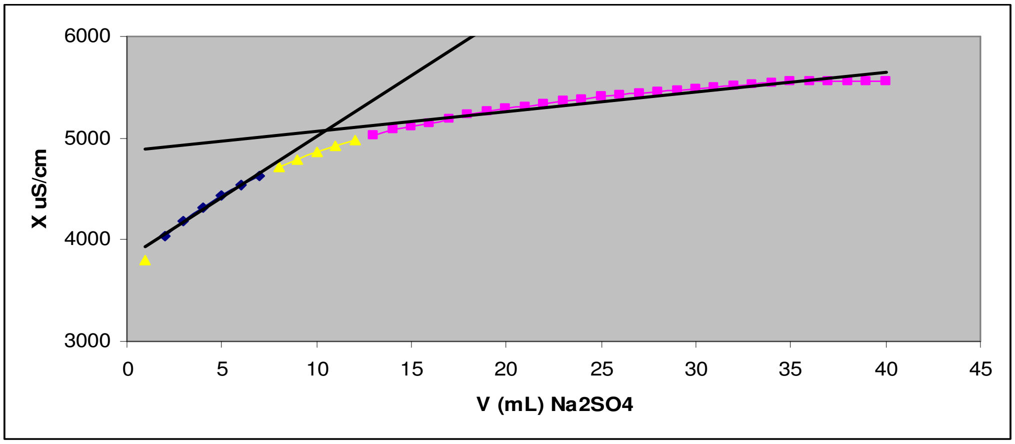

Figure A.24 : Titration 1x10^{-1} mol/L PSP with 1x10^{-1} mol/L Na_2SO_4, (I=1mol/L)

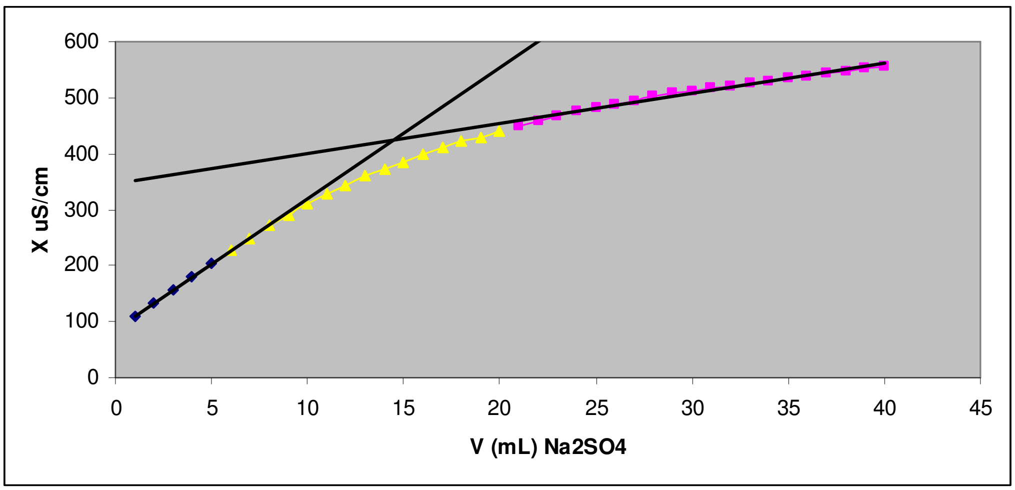

Figure A.25 : Titration 1x10^{-2} mol/L PSP with 1x10^{-2} mol/L Na_2SO_4
(I=10^{-1}mol/L)

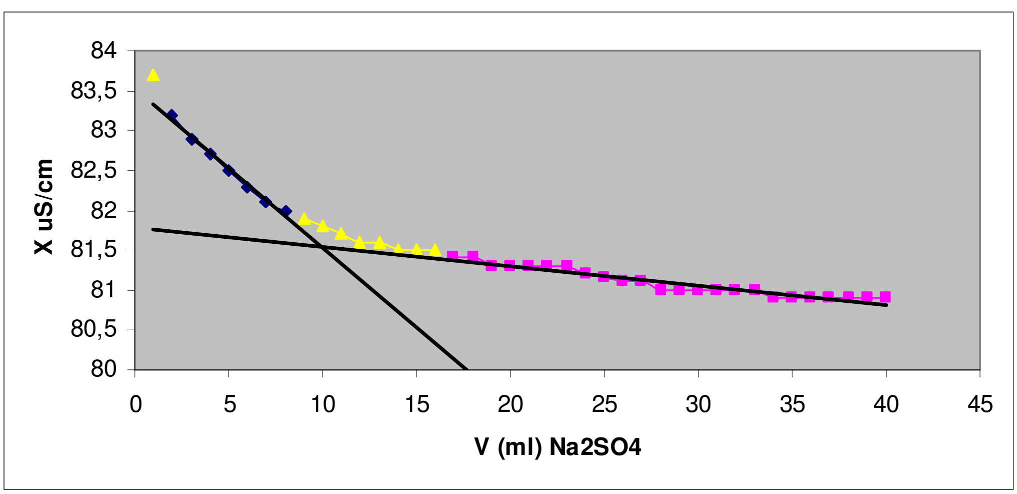

Figure A.26 : Titration 1x10^{-3} mol/L PSP with 1x10^{-3} mol/L Na_2SO_4,
(I=10^{-2}mol/L)

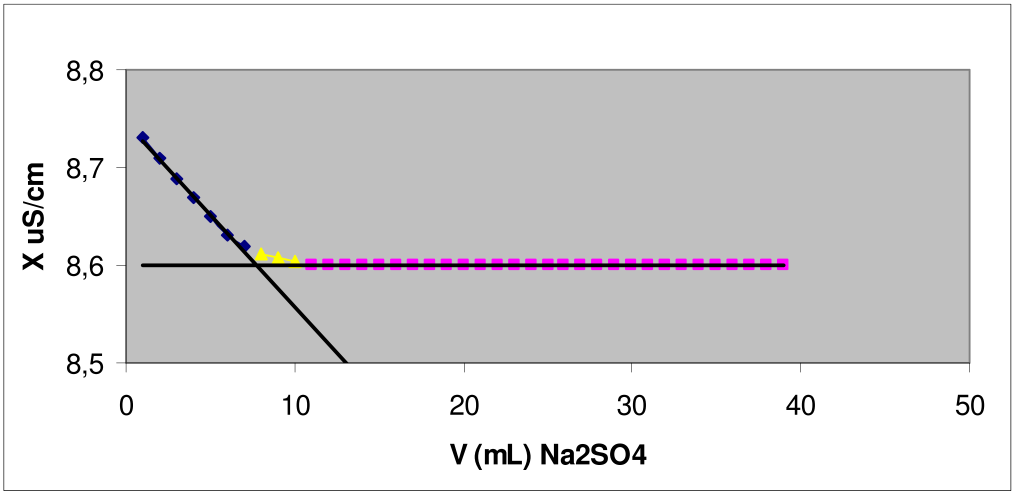

Figure A.27 : Titration 1x10^{-4} mol/L PSP with 1x10^{-4} mol/L Na_2SO_4, (I=10^{-3}mol/L)

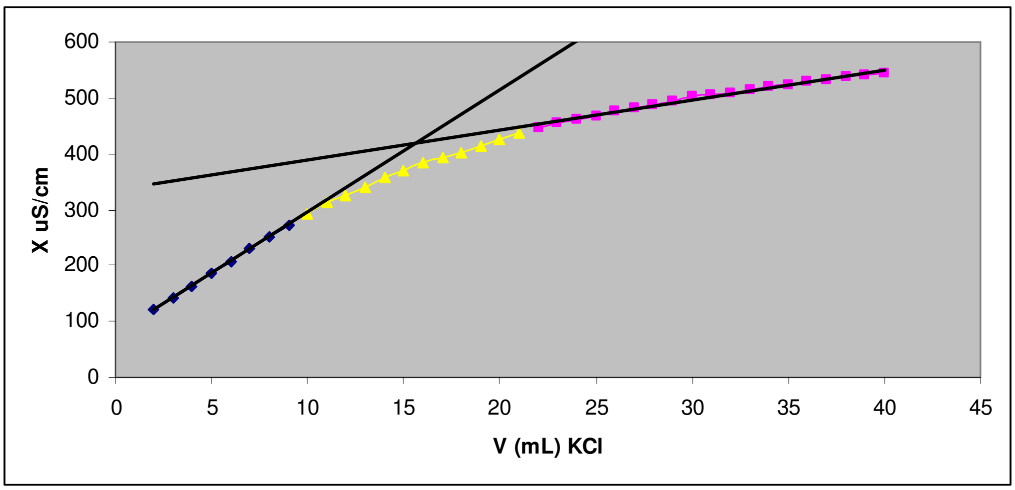

Figure A.28 : Titration 1x10^{-2} mol/L PSP with 1x10^{-2} mol/L KCl(I=10^{-1}mol/L)

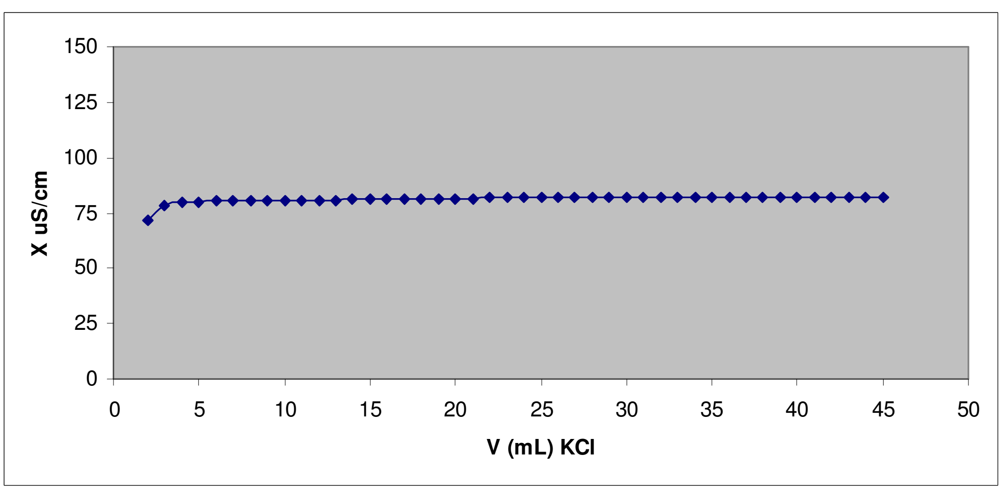

Figure A.29 : Titration 1x10^{-3} mol/L PSP with 1x10^{-3} mol/L KCl, (I=10^{-2}mol/L)

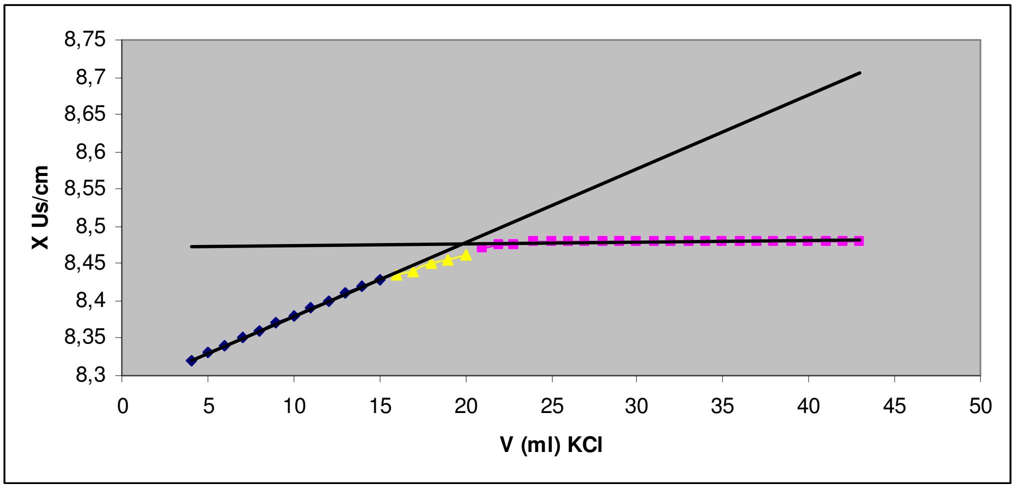

Figure A.30 : Titration 1x10^{-4} mol/L PSP with 1x10^{-4} mol/L KCl, (I=10^{-3}mol/L)

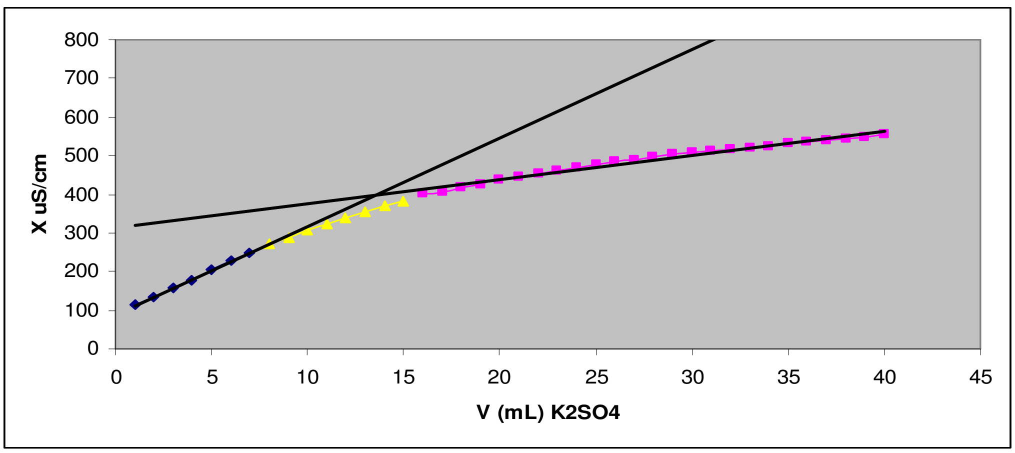

Figure A.31 : Titration 1x10^{-2} mol/L PSP with 1x10^{-2} mol/L K_2SO_4, (I=10^{-1}mol/L)

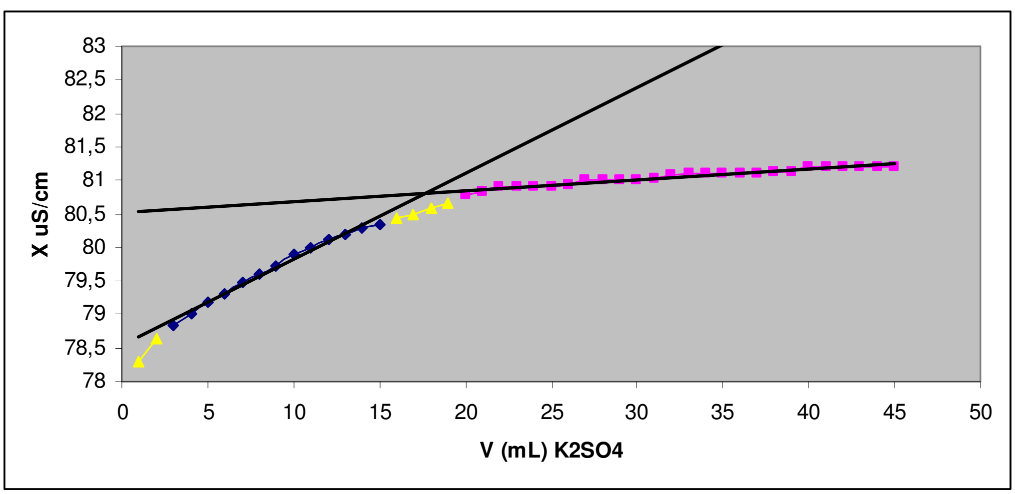

Figure A.32 : Titration 1x10^{-3} mol/L PSP with 1x10^{-3} mol/L K_2SO_4, (I=10^{-2}mol/L)

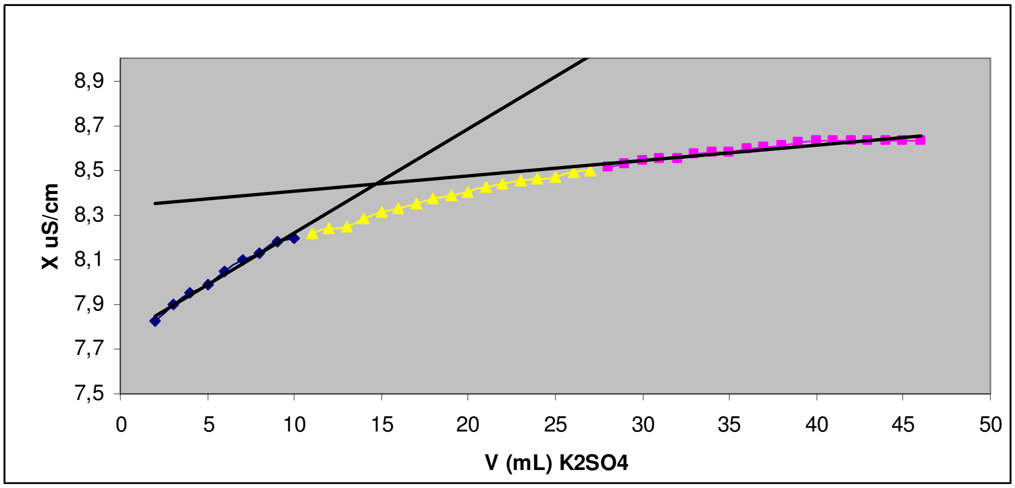

Figure A.33 : Titration 1x10^{-4} mol/L PSP with 1x10^{-4} mol/L K_2SO_4, (I=10^{-3}mol/L)

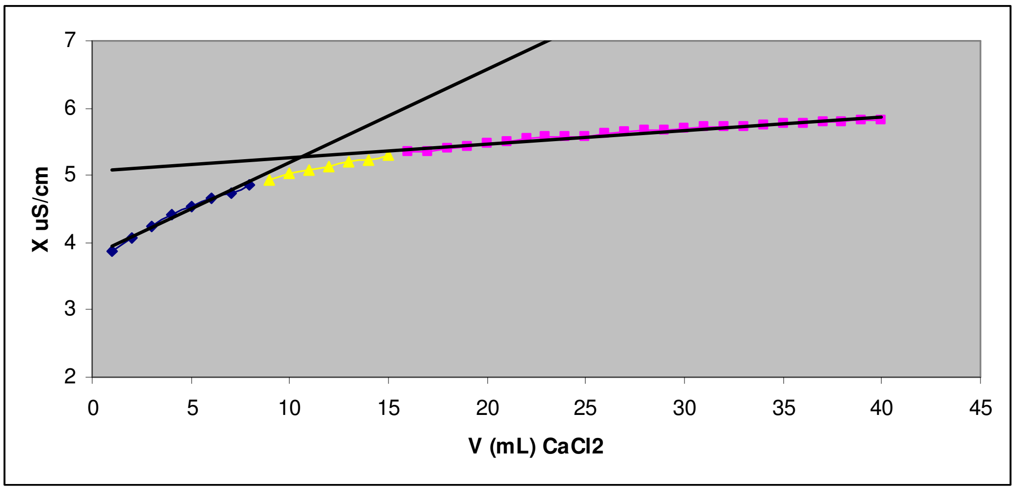

Figure A.34 : Titration 1x10^{-1} mol/L PSP with 1x10^{-1} mol/L $CaCl_2$, (I=1 mol/L)

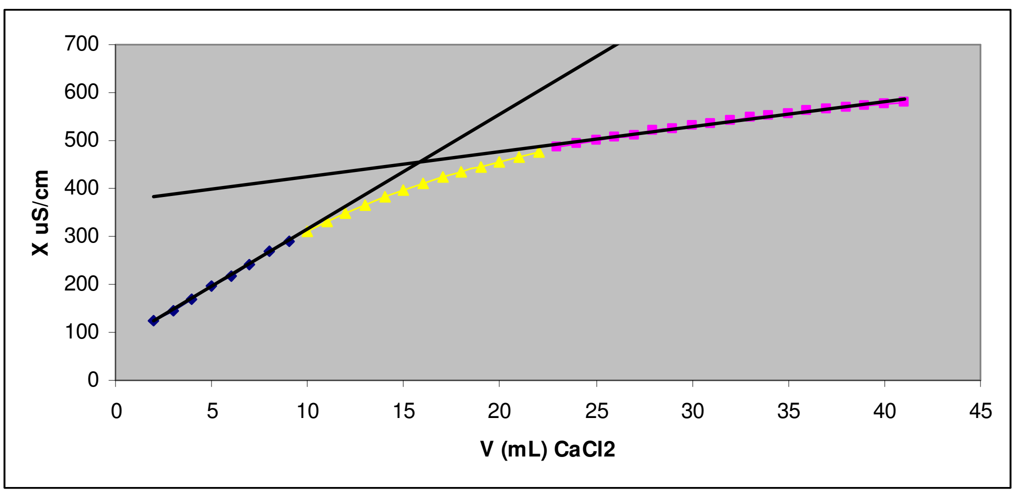

Figure A.35 : Titration 1x10^{-2} mol/L PSP with 1x10^{-2} mol/L $CaCl_2$, (I=10^{-1}mol/L)

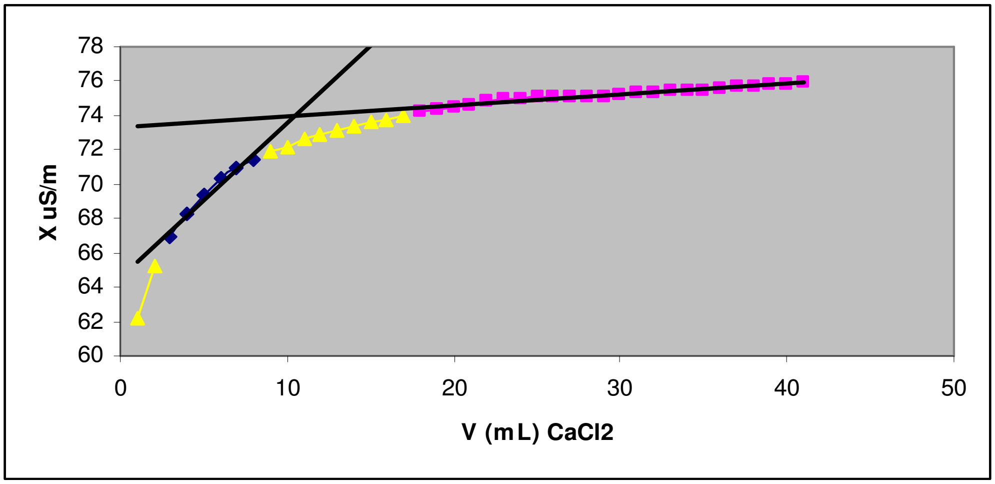

Figure A.36 : Titration 1x10^{-3} mol/L PSP with 1x10^{-3} mol/L $CaCl_2$, (I=10^{-2}mol/L)

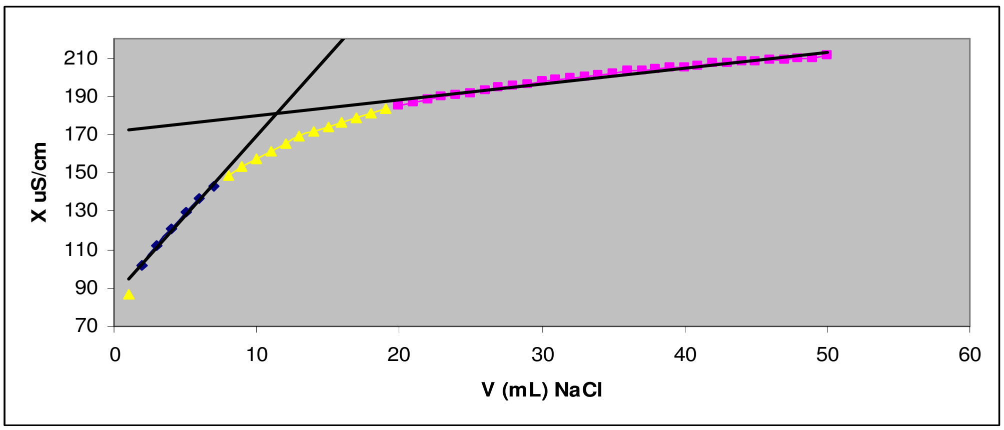

Figure A.37 : Titration 1x10^{-1} mol/L PAH with 1x10^{-1} mol/L NaCl

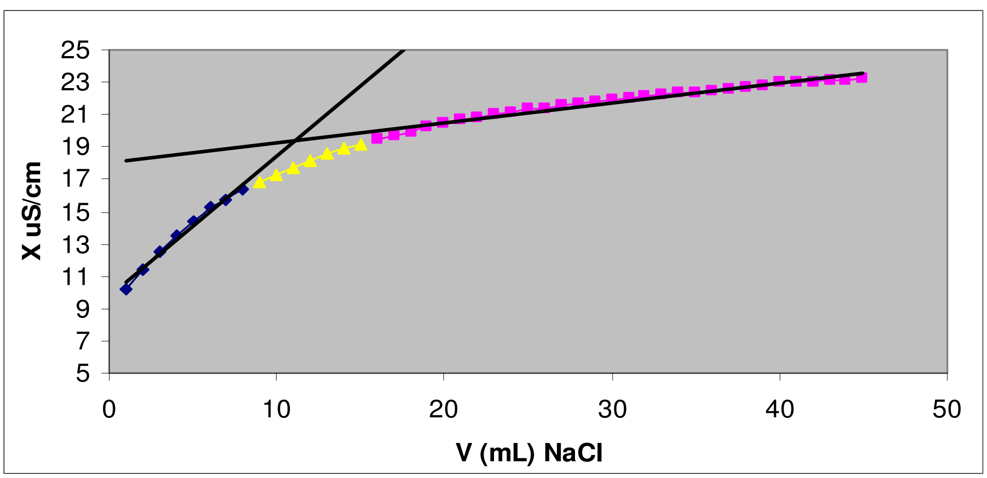

Figure A.38 : Titration 1x10^{-2} mol/L PAH with 1x10^{-2} mol/L NaCl

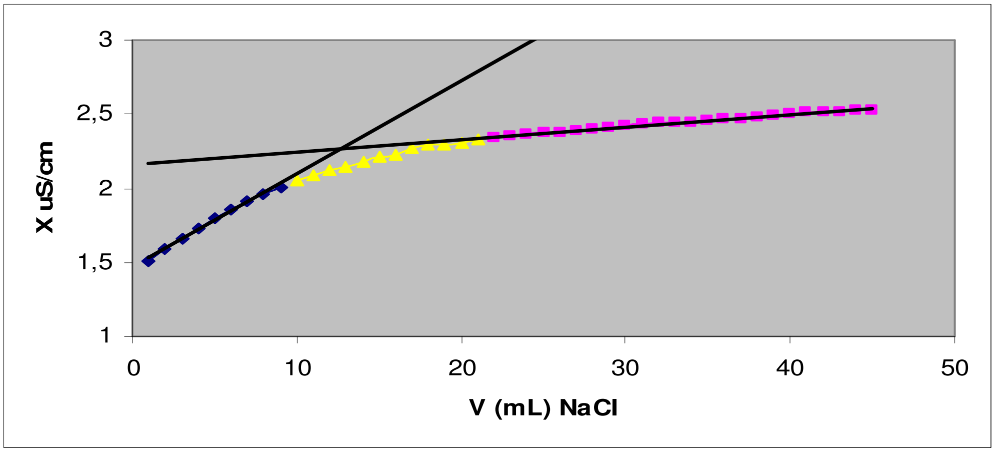

Figure A.39 : Titration 1x10^{-3} mol/L PAH with 1x10^{-3} mol/L NaCl

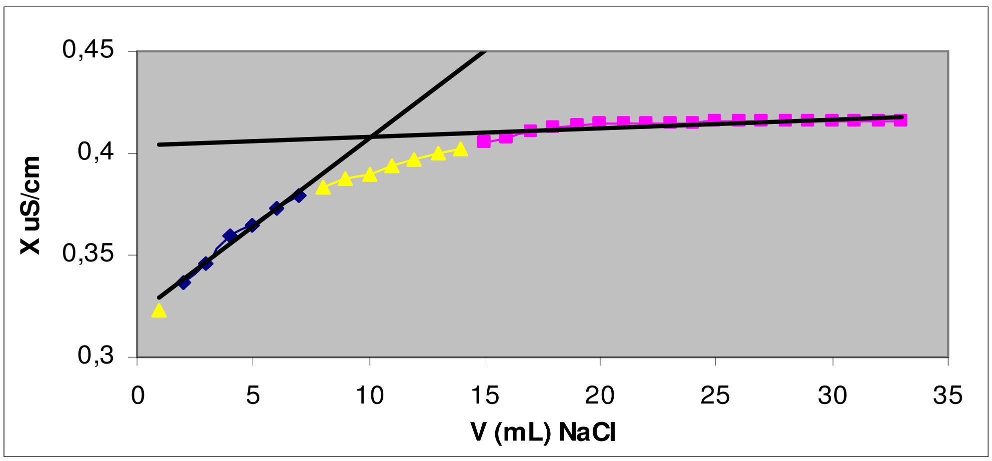

Figure A.40 : Titration 1x10^{-4} mol/L PAH with 1x10^{-4} mol/L NaCl

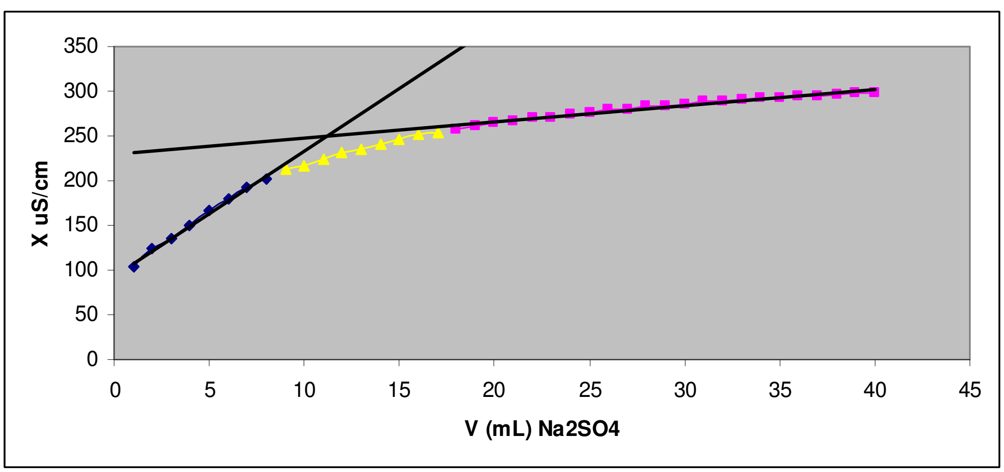

Figure A.41 : Titration 1x10^{-1} mol/L PAH with 1x10^{-1} mol/L Na_2SO_4

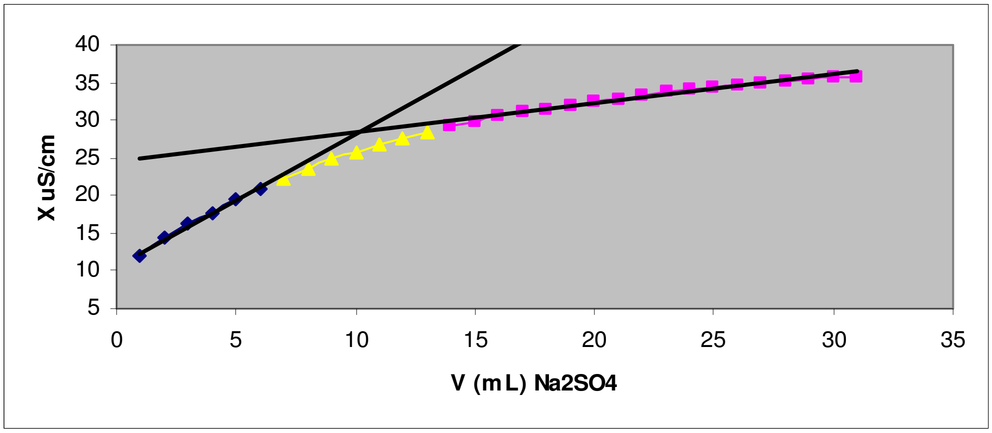

Figure A.42 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L Na_2SO_4

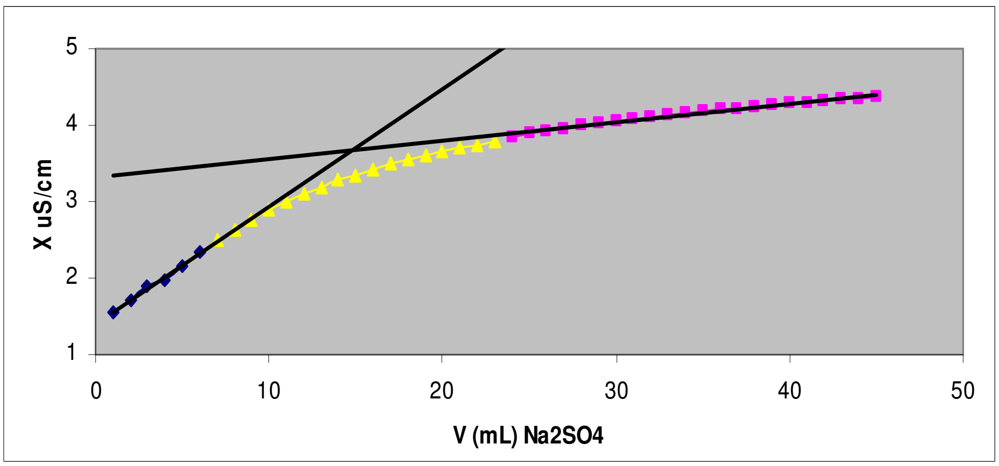

Figure A.43 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L Na_2SO_4

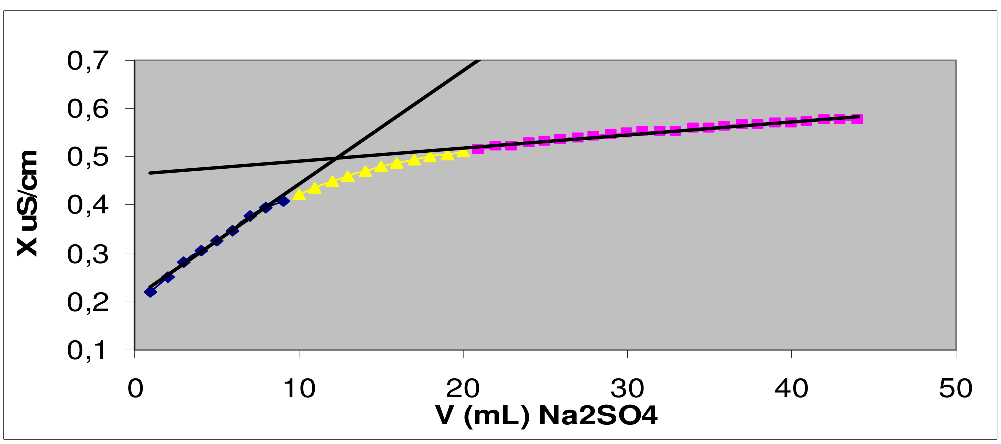

Figure A.44 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L Na_2SO_4

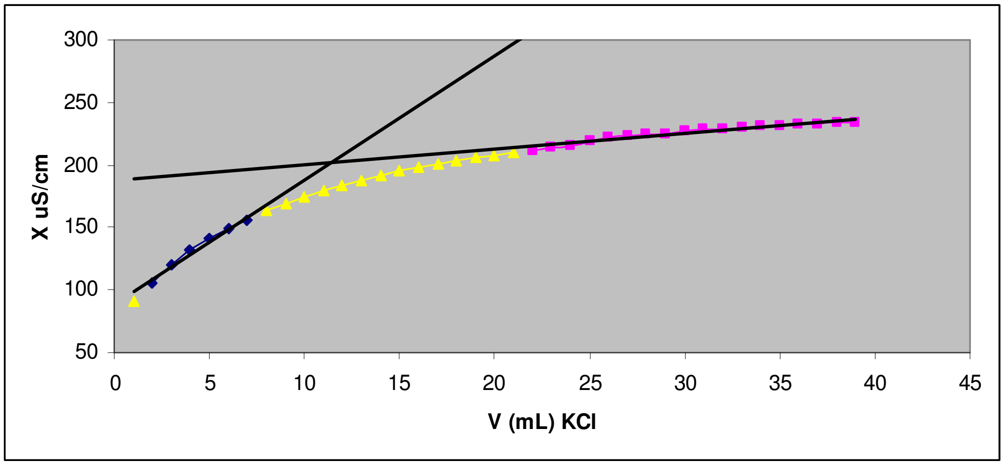

Figure A.45 : Titration 1x10^{-1} mol/L PAH with 1x10^{-1} mol/L KCl

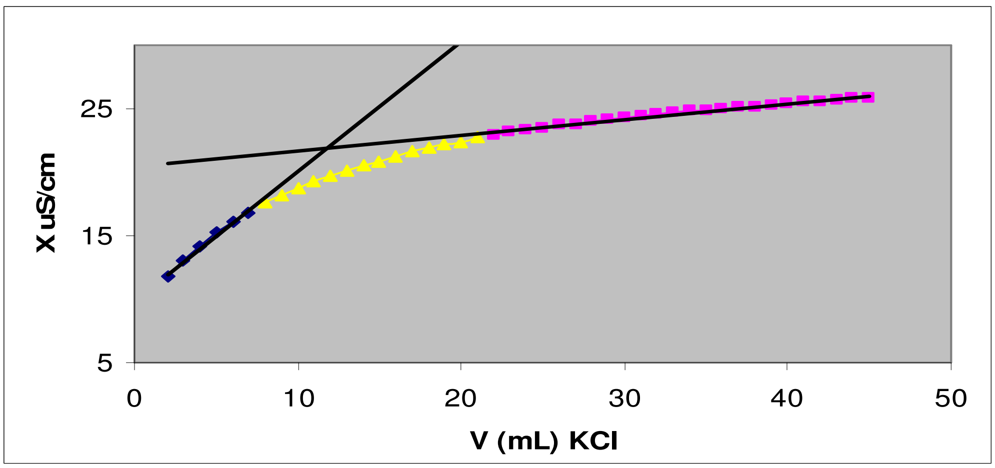

Figure A.46 : Titration 1x10^{-2} mol/L PAH with 1x10^{-2} mol/L KCl

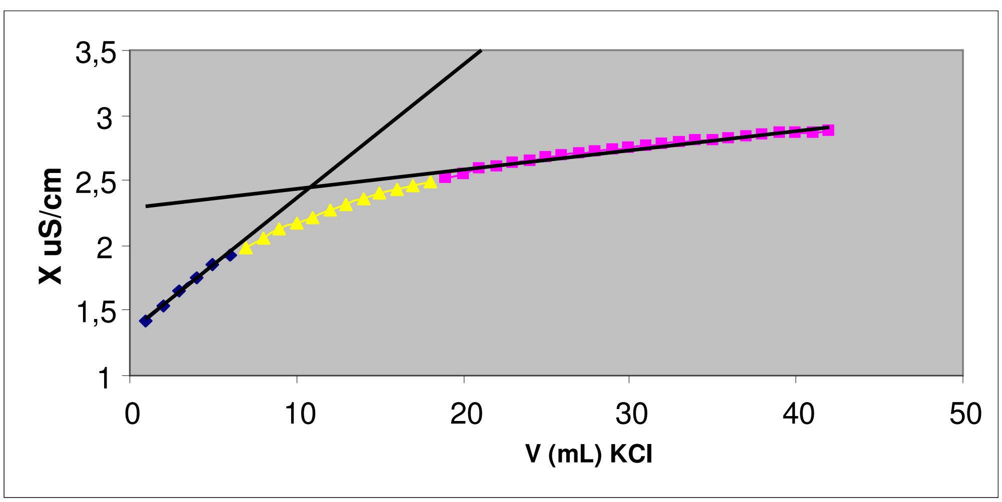

Figure A.47 : Titration 1x10^{-3} mol/L PAH with 1x10^{-3} mol/L KCl

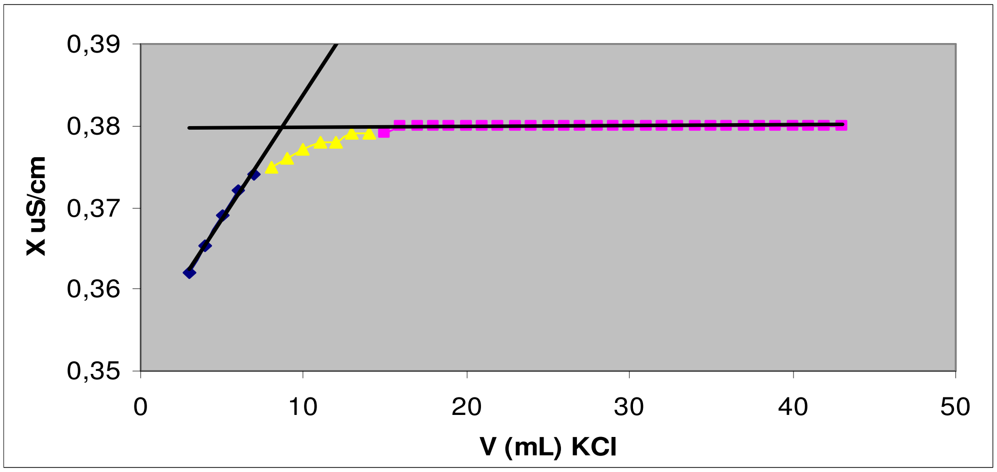

Figure A.48 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L KCl

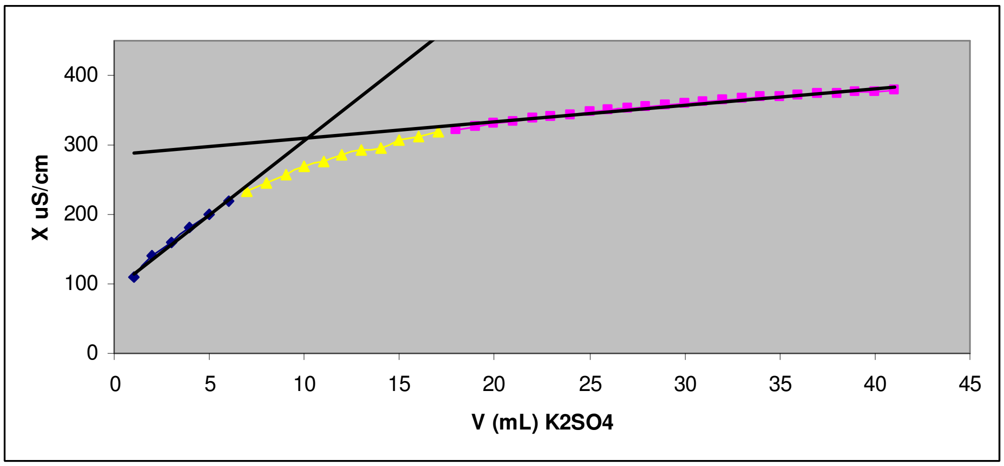

Figure A.49 : Titration $1x10^{-1}$ mol/L PAH with $1x10^{-1}$ mol/L K_2SO_4

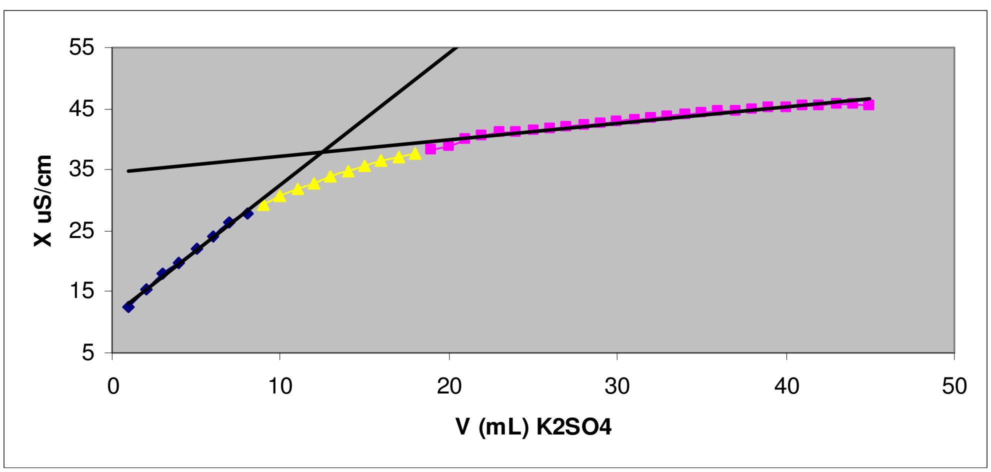

Figure A.50 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L K_2SO_4

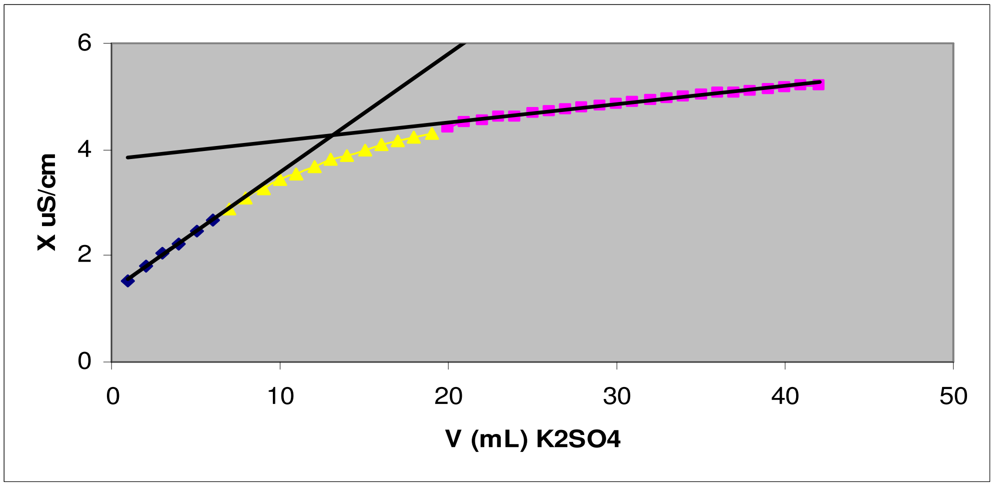

Figure A.51 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L K_2SO_4

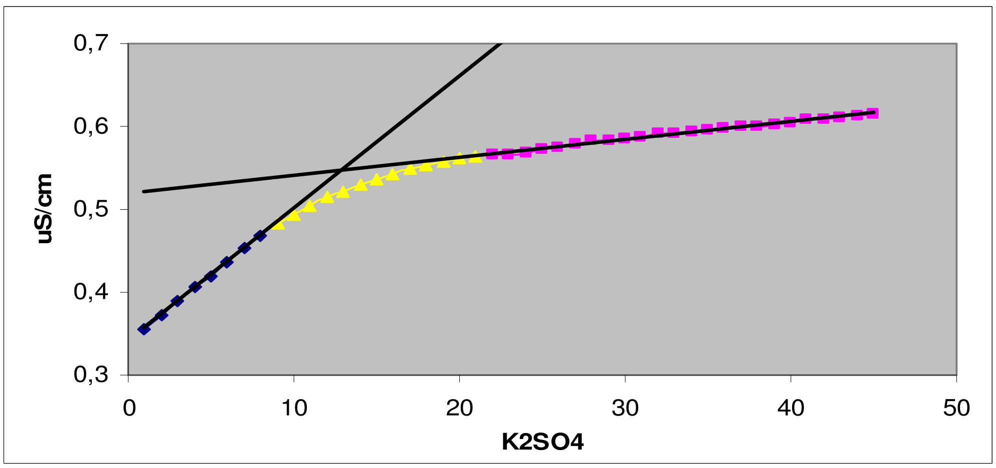

Figure A.52 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L K_2SO_4

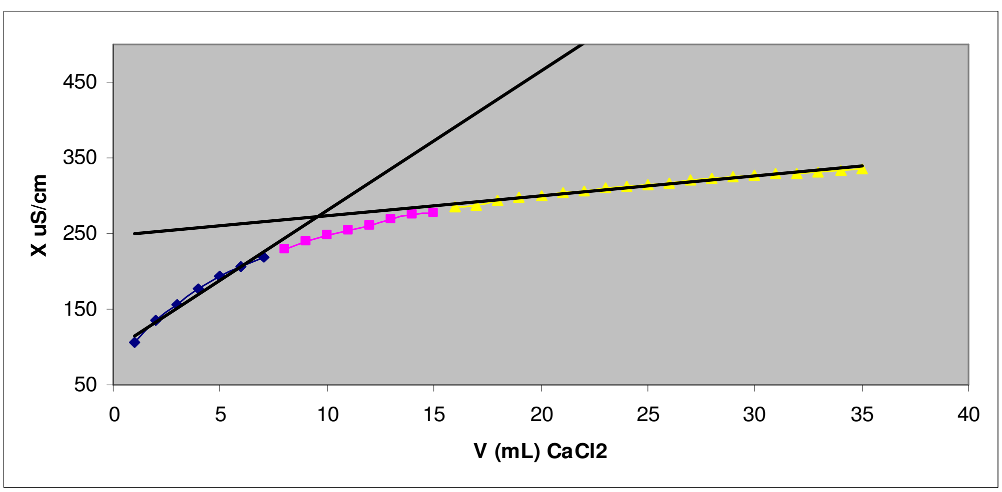

Figure A.53 : Titration $1x10^{-1}$ mol/L PAH with $1x10^{-1}$ mol/L $CaCl_2$

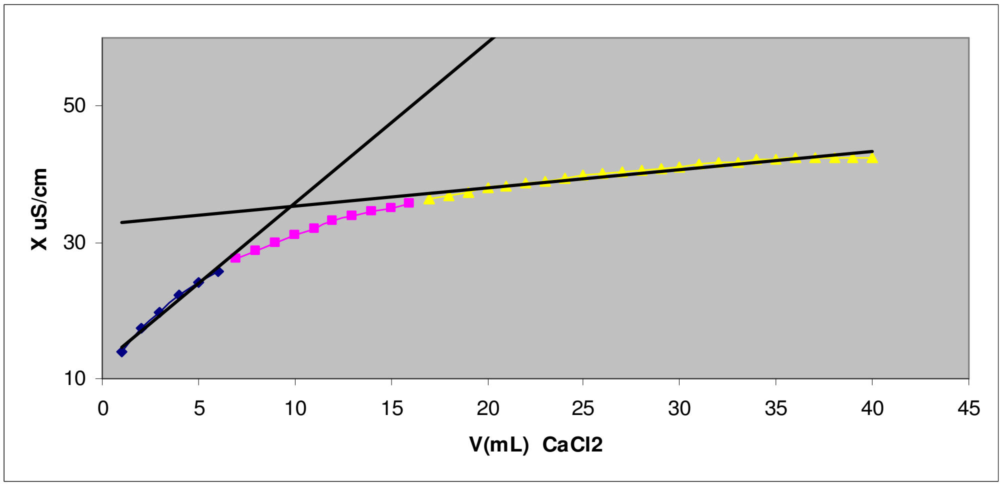

Figure A.54 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L $CaCl_2$

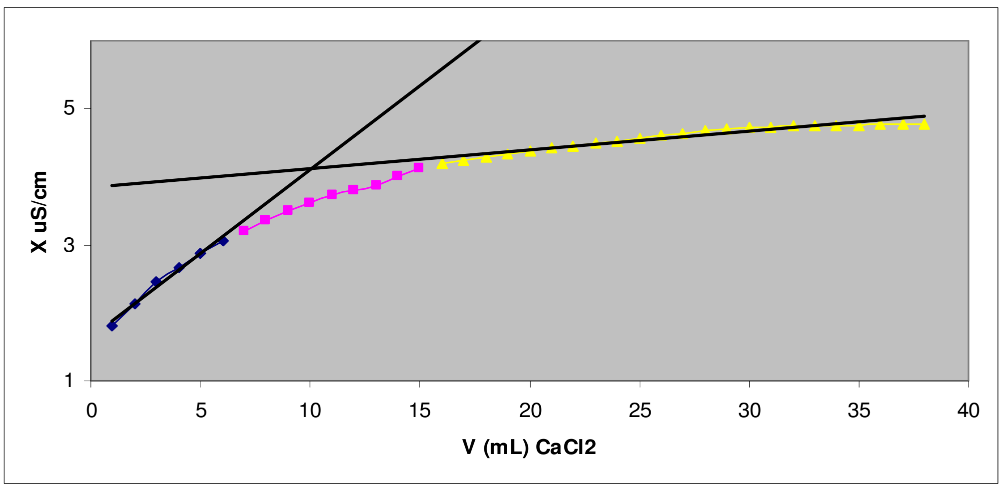

Figure A.55 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L $CaCl_2$

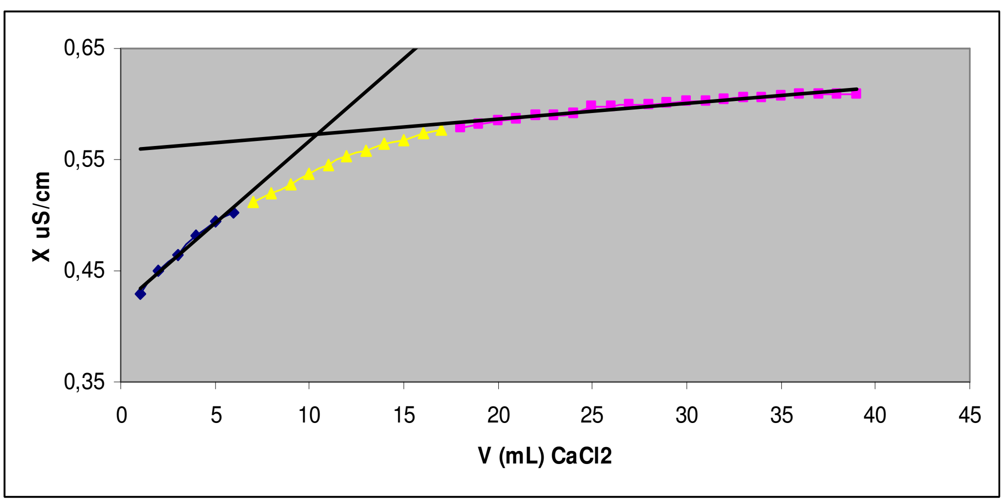

Figure A.56 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L $CaCl_2$

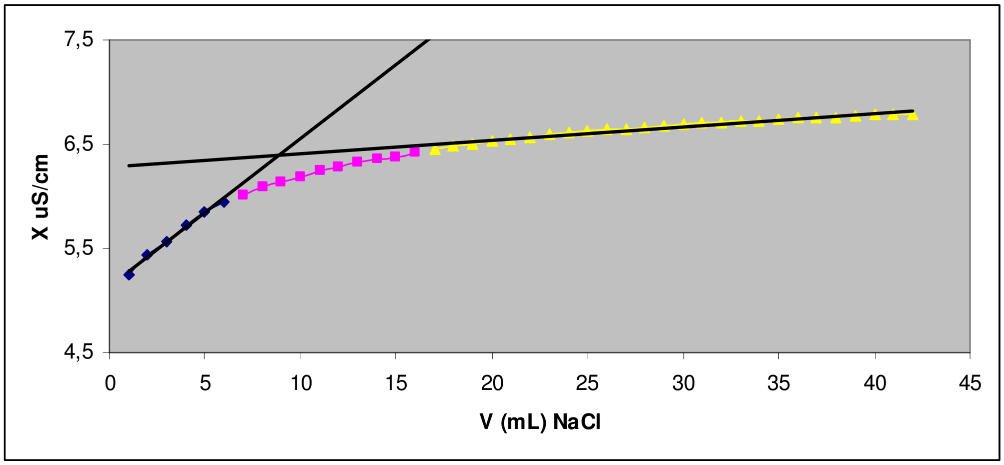

Figure A.57 : Titration 1x10^{-1} mol/L PAH with 1x10^{-1} mol/L NaCl, (I=1 mol/L)

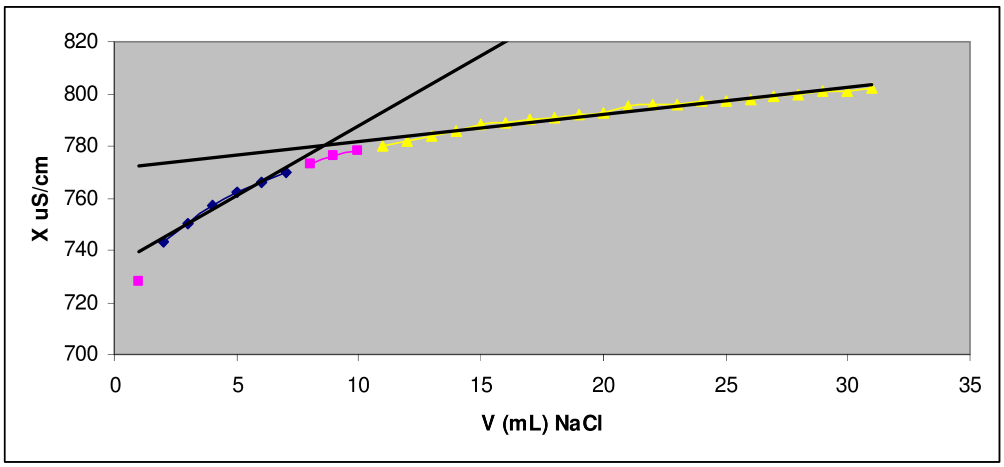

Figure A.58 : Titration 1x10^{-2} mol/L PAH with 1x10^{-2} mol/L NaCl, (I=1x10^{-1} mol/L)

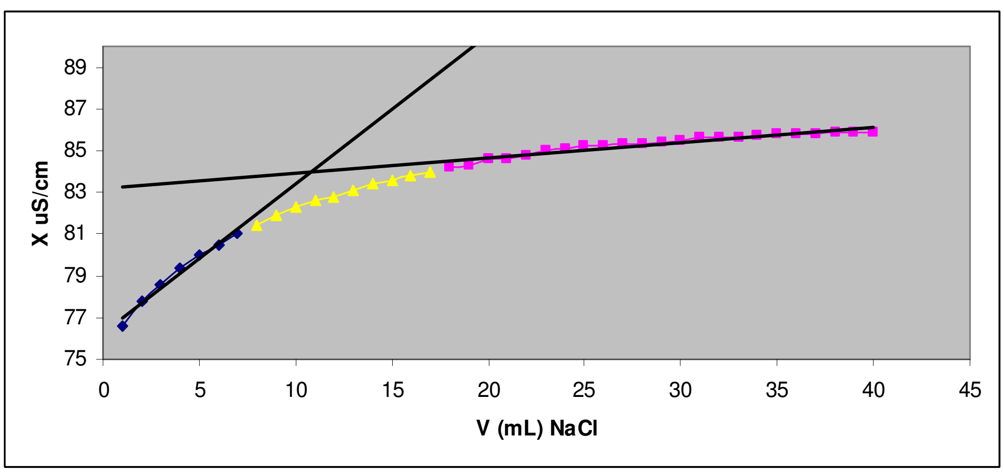

Figure A.59 : Titration 1x10^{-3} mol/L PAH with 1x10^{-3} mol/L NaCl, (I=1x10^{-2} mol/L)

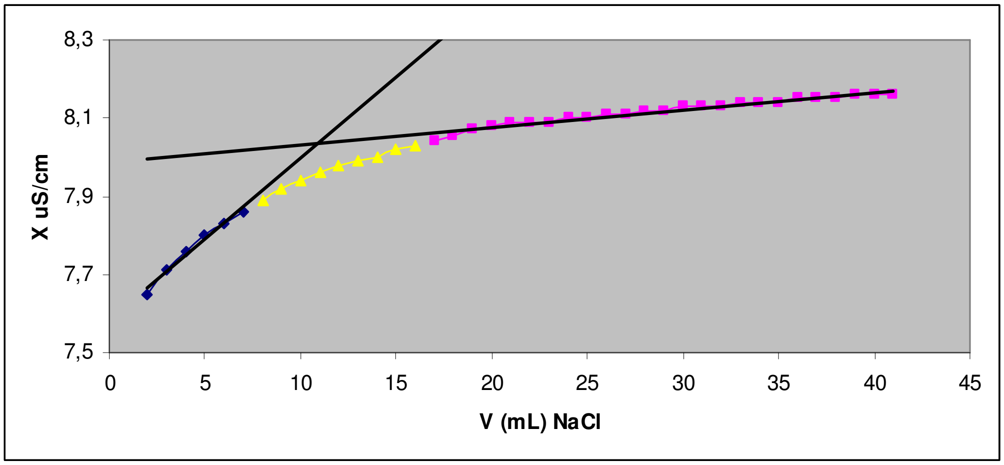

Figure A.60 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L NaCl, ($I=1x10^{-3}$ mol/L)

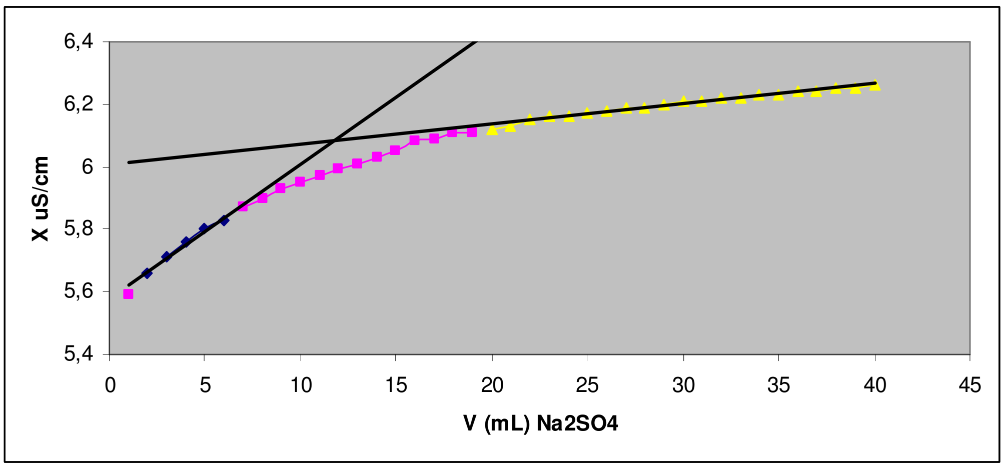

Figure A.61 : Titration $1x10^{-1}$ mol/L PAH with $1x10^{-1}$ mol/L Na_2SO_4, (I=1 mol/L)

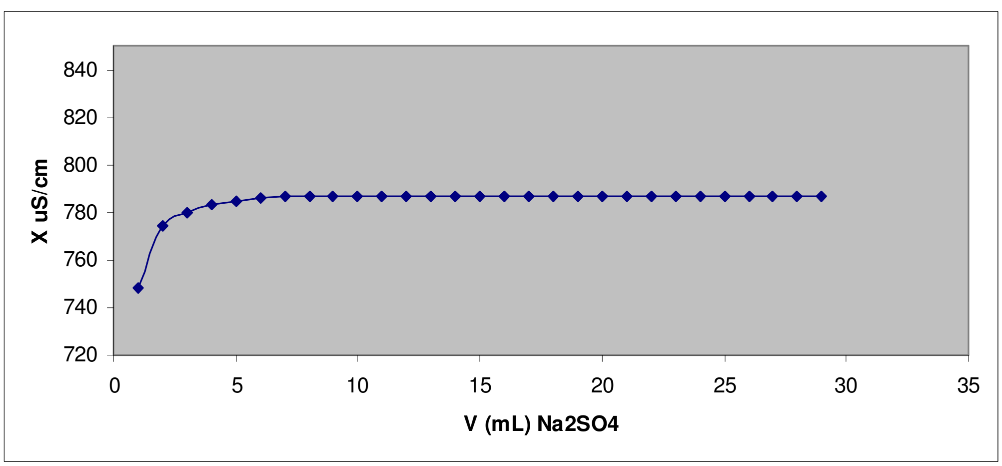

Figure A.62 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L Na_2SO_4, ($I=1x10^{-1}$ mol/L)

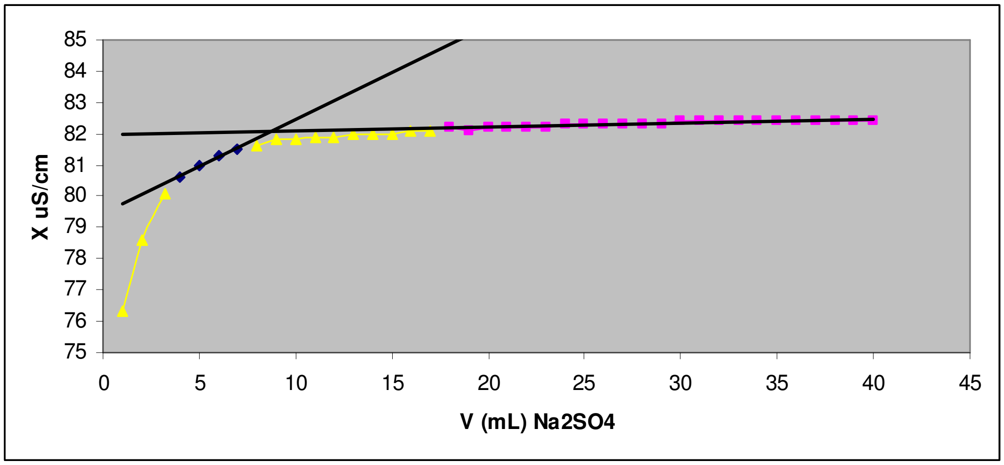

Figure A.63 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L Na_2SO_4, ($I=1x10^{-2}$ mol/L)

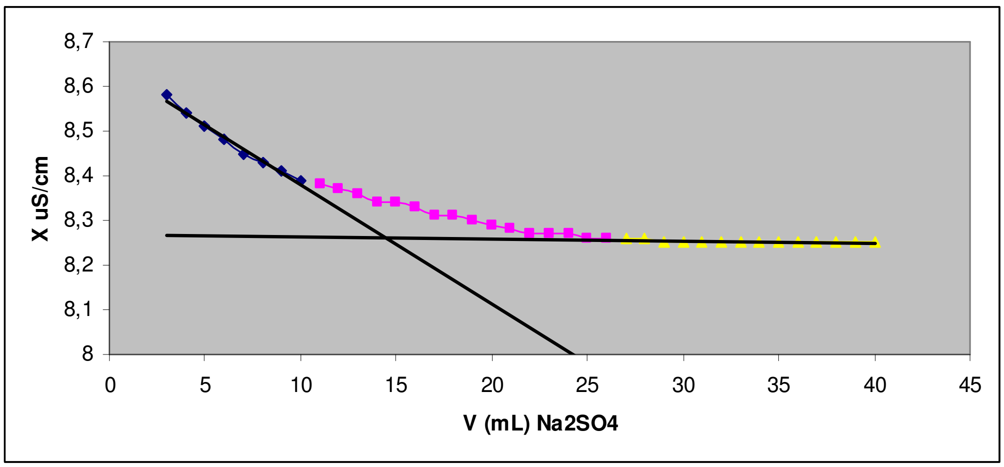

Figure A.64 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L Na_2SO_4, ($I=1x10^{-3}$ mol/L)

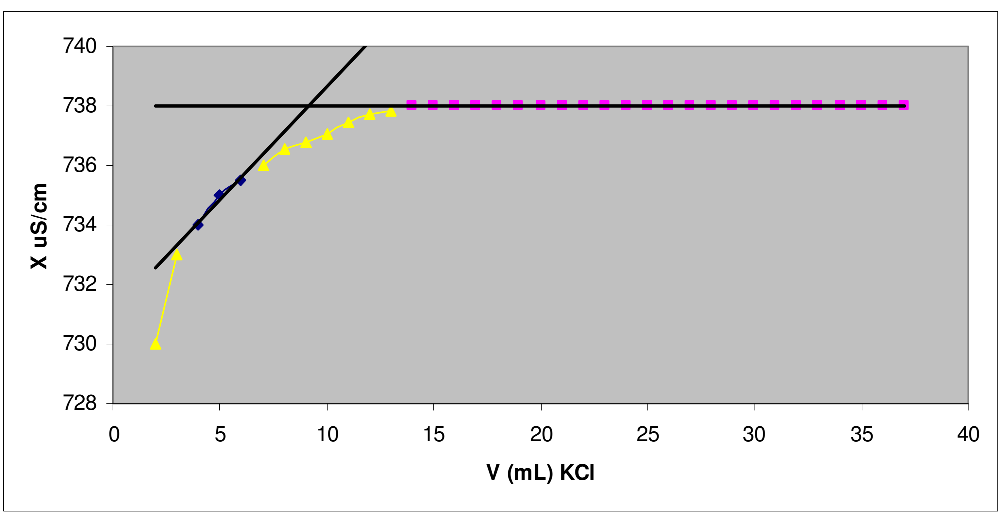

Figure A.65 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L KCl, ($I=1x10^{-1}$ mol/L)

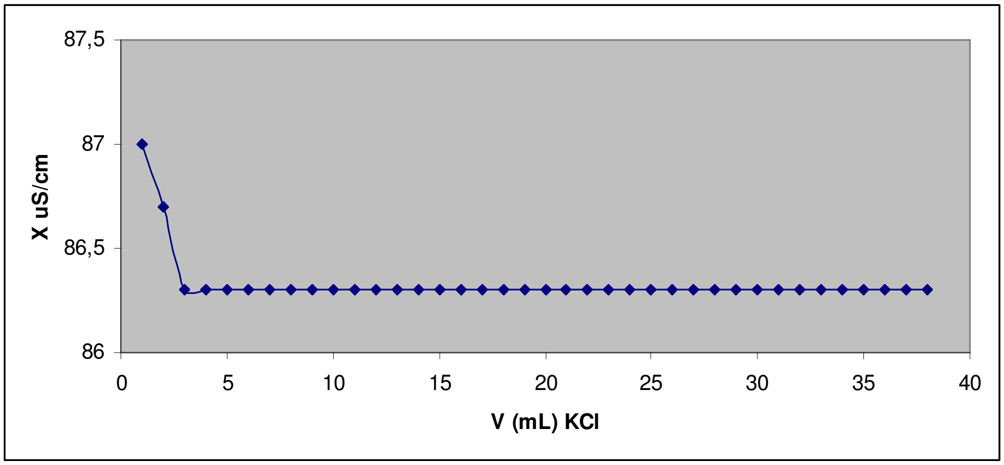

Figure A.66 : Titration 1x10^{-3} mol/L PAH with 1x10^{-3} mol/L KCl, (I=1x10^{-2} mol/L)

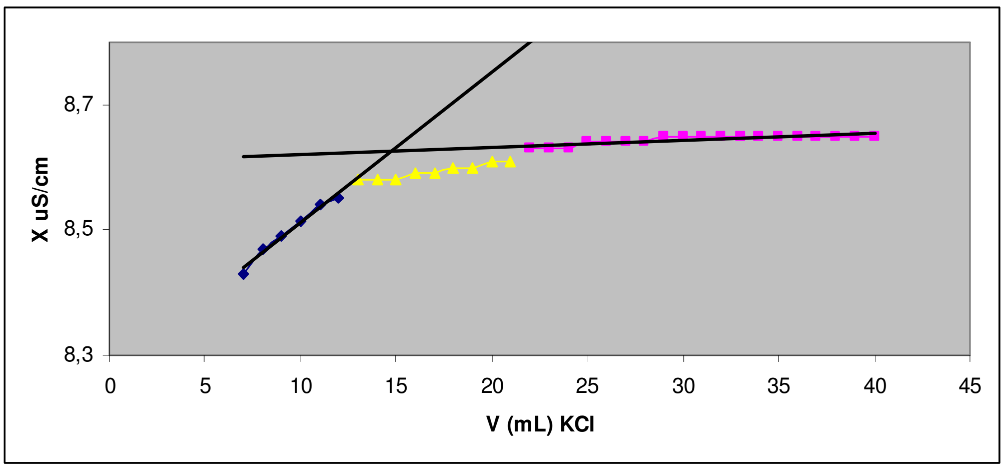

Figure A.67 : Titration 1x10^{-4} mol/L PAH with 1x10^{-4} mol/L KCl, (I=1x10^{-3} mol/L)

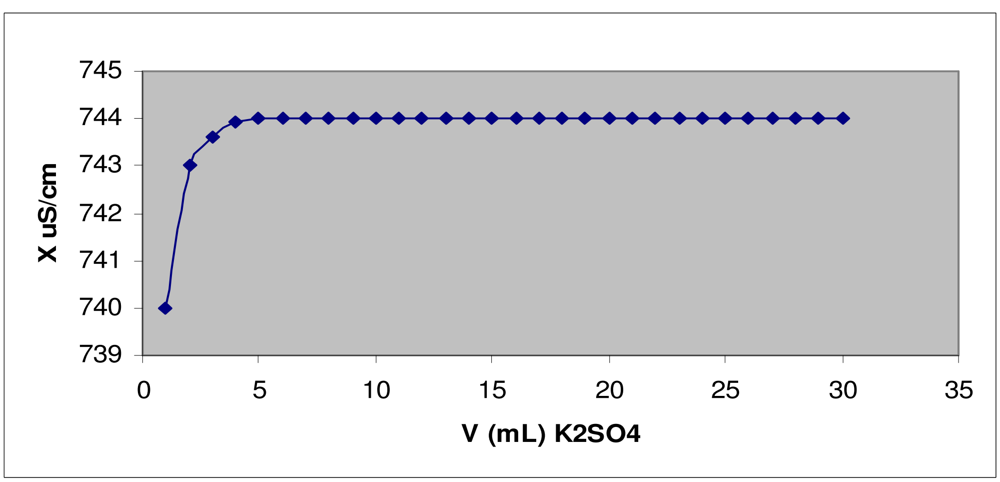

Figure A.68 : Titration 1x10^{-2} mol/L PAH with 1x10^{-2} mol/L K_2SO_4, (I=1x10^{-1} mol/L)

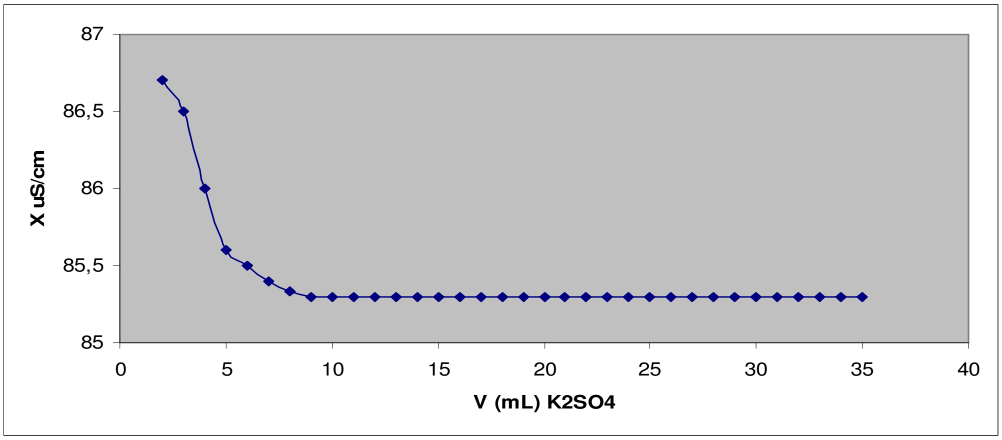

Figure A.69 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L K_2SO_4, ($I=1x10^{-2}$ mol/L)

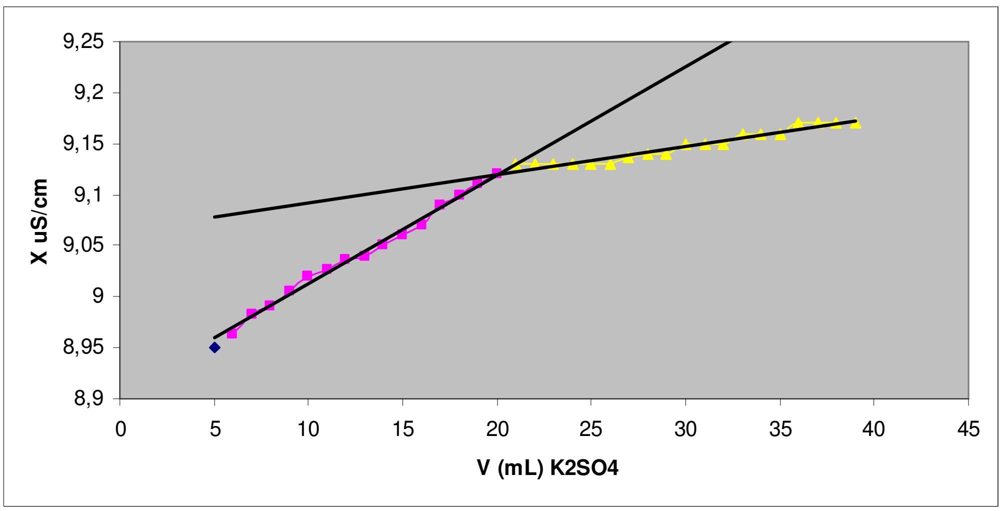

Figure A.70 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L K_2SO_4, ($I=1x10^{-3}$ mol/L)

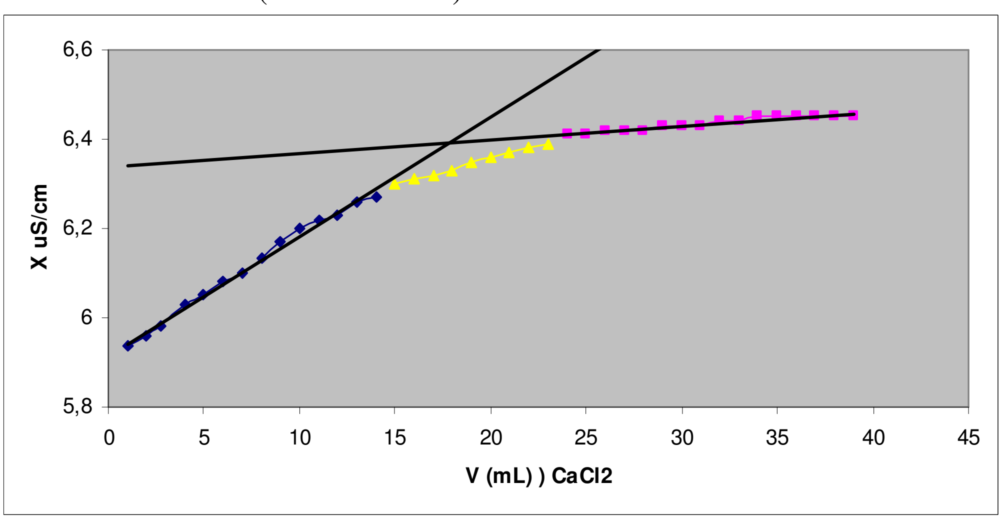

Figure A.71 : Titration $1x10^{-1}$ mol/L PAH with $1x10^{-1}$ mol/L $CaCl_2$, ($I=1$mol/L)

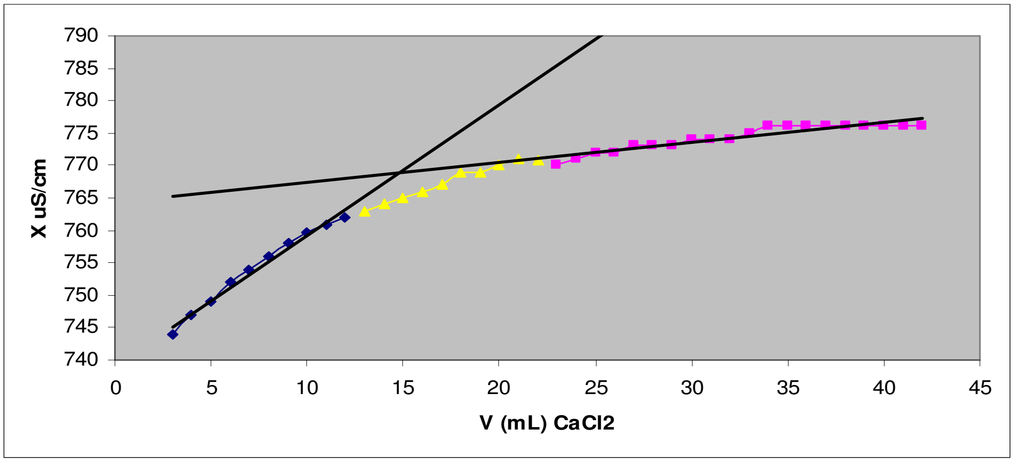

Figure A.72 : Titration $1x10^{-2}$ mol/L PAH with $1x10^{-2}$ mol/L $CaCl_2$, ($I=1x10^{-1}$ mol/L)

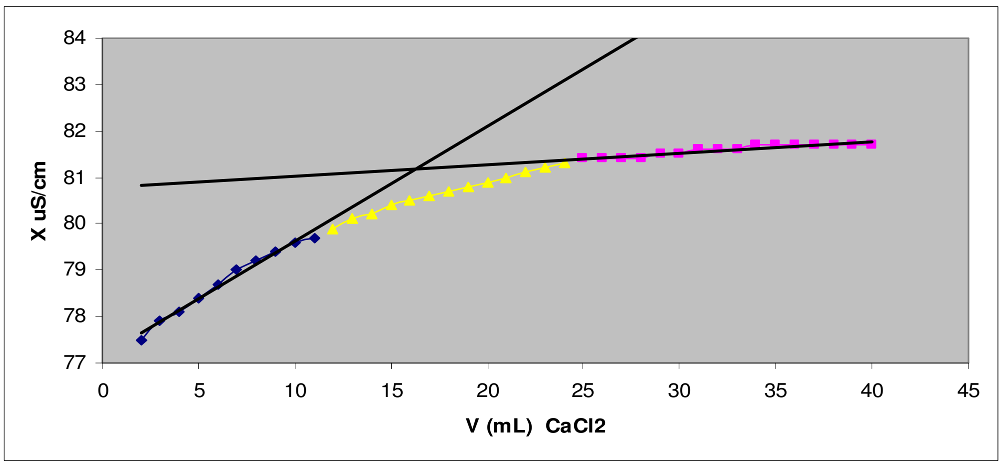

Figure A.73 : Titration $1x10^{-3}$ mol/L PAH with $1x10^{-3}$ mol/L $CaCl_2$, ($I=1x10^{-2}$ mol/L)

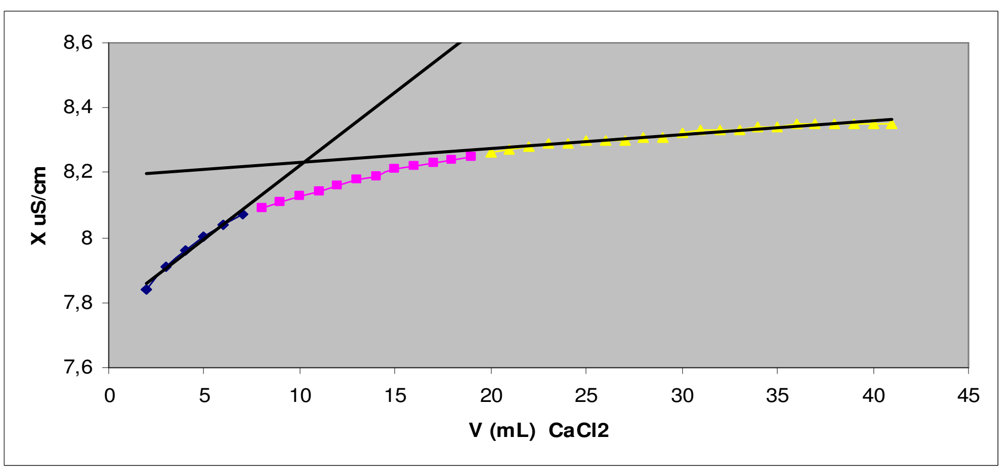

Figure A.74 : Titration $1x10^{-4}$ mol/L PAH with $1x10^{-4}$ mol/L $CaCl_2$, ($I=1x10^{-3}$ mol/L)

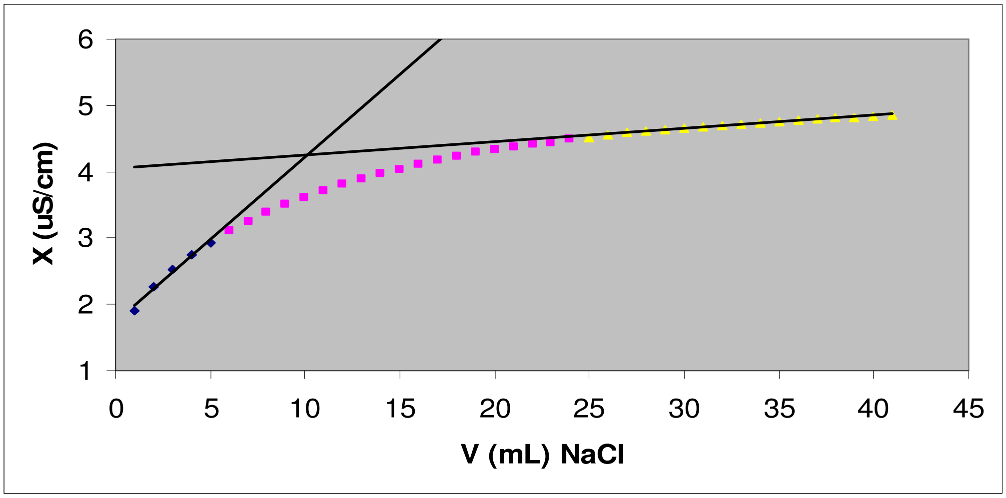

Figure A.75 : Titration of 0.102mg/mL PSP with NaCl (I=varied)

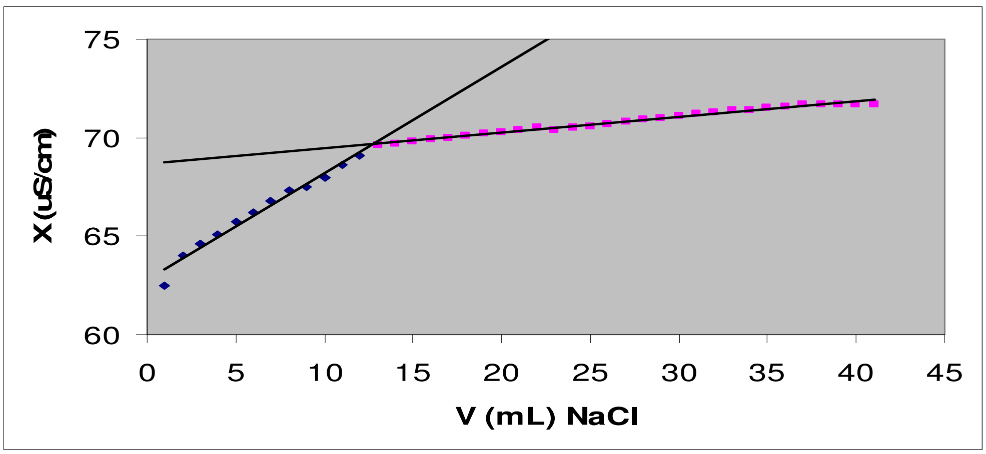

Figure A.76 : Titration of 0.102mg/mL PSP with NaCl (I=1x10^{-2}mol/L)

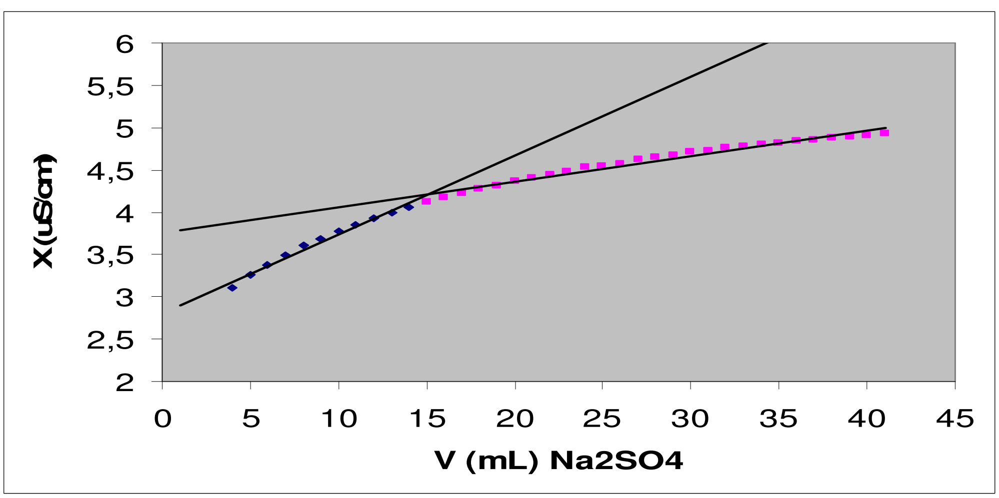

Figure A.77 : Titration of 0.142mg/mL PSP with Na_2SO_4 (I=varied)

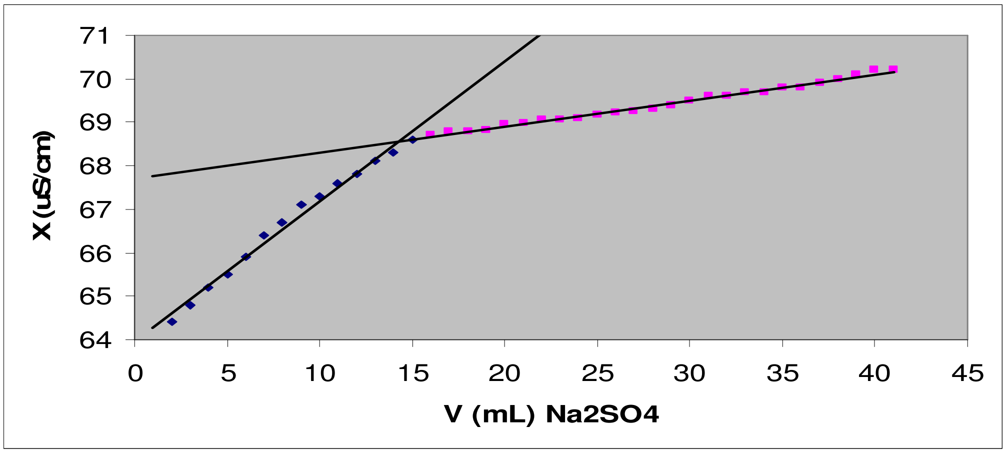

Figure A.78 : Titration of 0.142mg/mL PSP with Na_2SO_4 (I=1x10^{-2}mol/L)

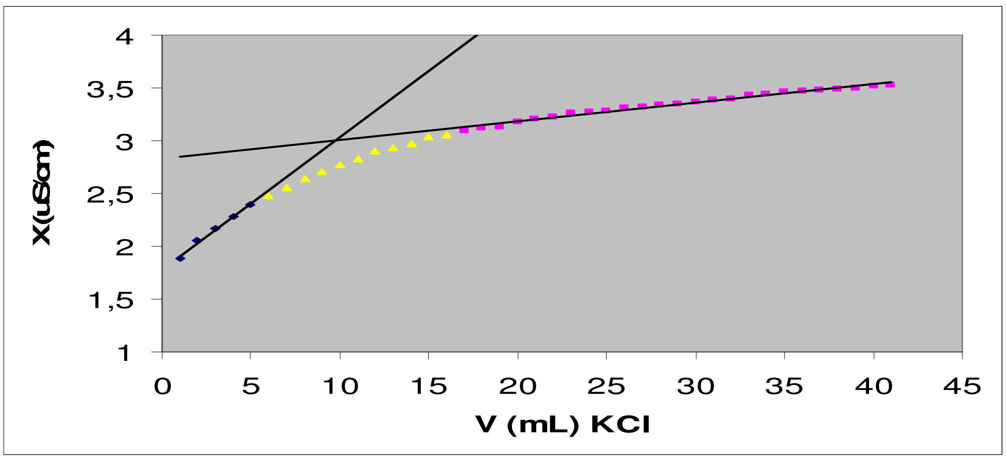

Figure A.79 : Titration of 0.102mg/mL PSP with KCl (I=varied)

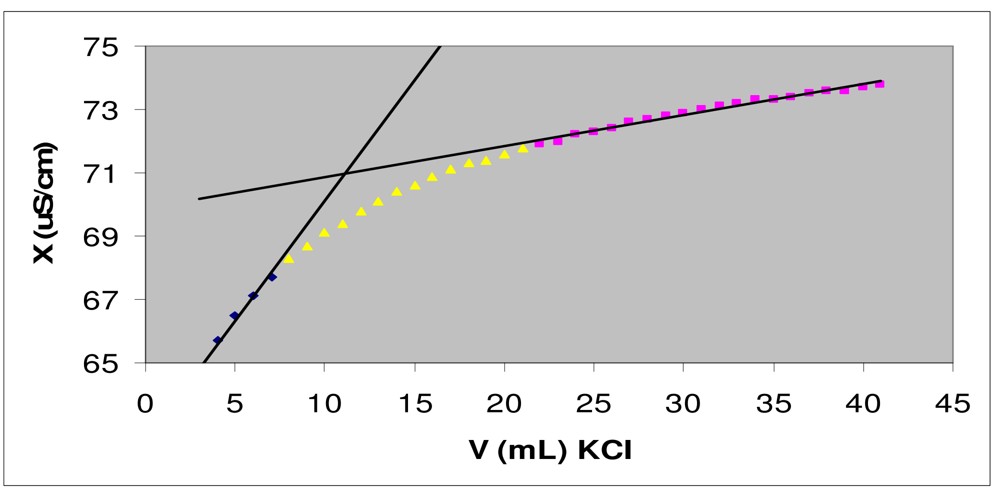

Figure A.80 : Titration of 0.102mg/mL PSP with KCl (I=1x10^{-2}mol/L)

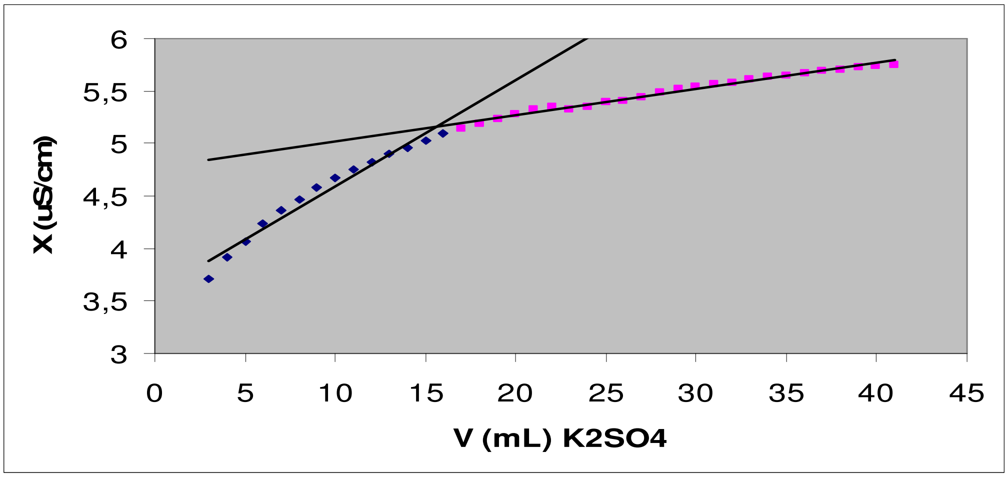

Figure A.81 : Titration of 0.174mg/mL PSP with K_2SO_4 (I=varied)

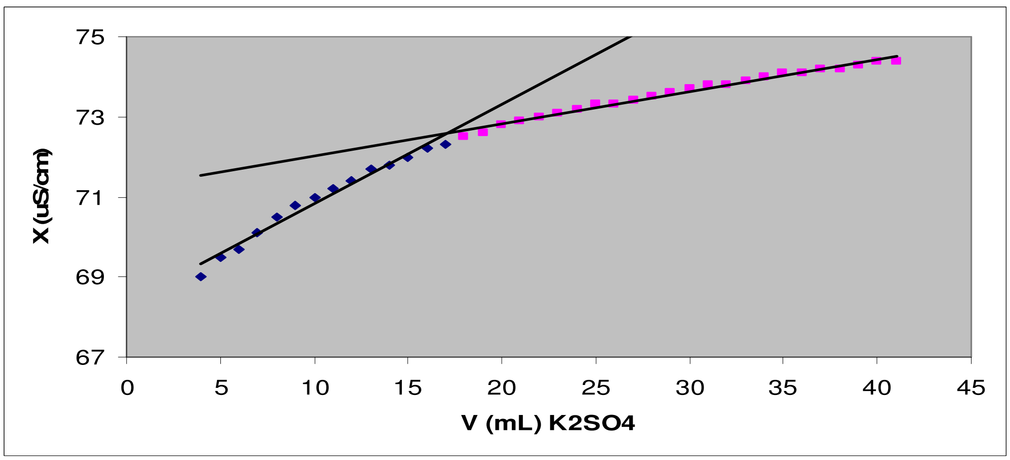

Figure A.82 : Titration of 0.174mg/mL PSP with K_2SO_4 (I=1x10^{-2}mol/L)

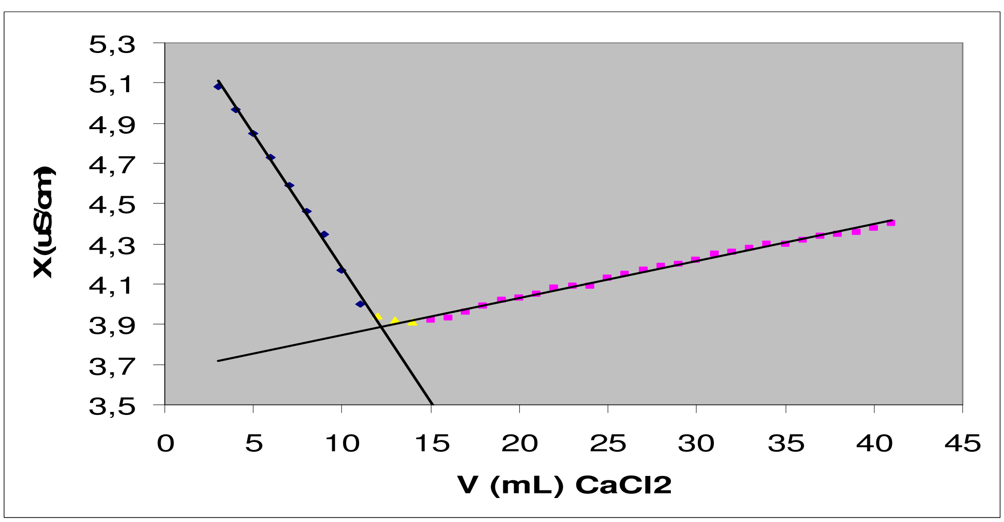

Figure A.83 : Titration of 0.219mg/mL PSP with $CaCl_2$ (I=varied)

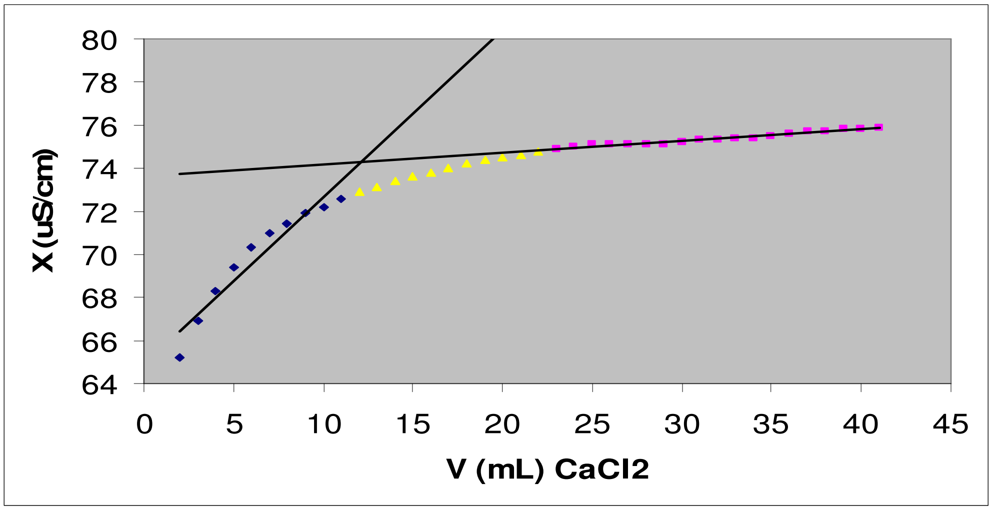

Figure A.84 : Titration of 0.219mg/mL PSP with $CaCl_2$ (I=1x10^{-2}mol/L)

APPENDİX B: Figures of Thermodynamic Results for PSP-Salt (I=Varied)

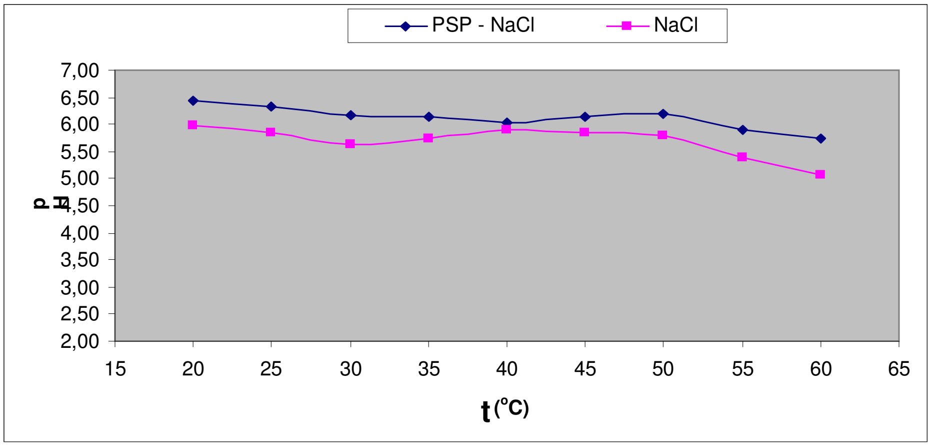

Figure B.1 : pH=f(t °C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) NaCl

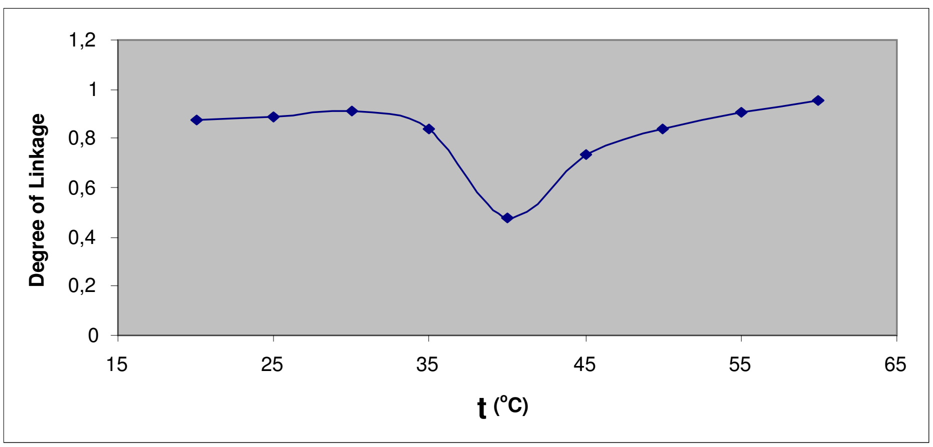

Figure B.2 : Degree of linkage, θ =f(t °C) Curve of $1x10^{-1}$(mo/L) PSP – $1x10^{-1}$(mo/L) NaCl

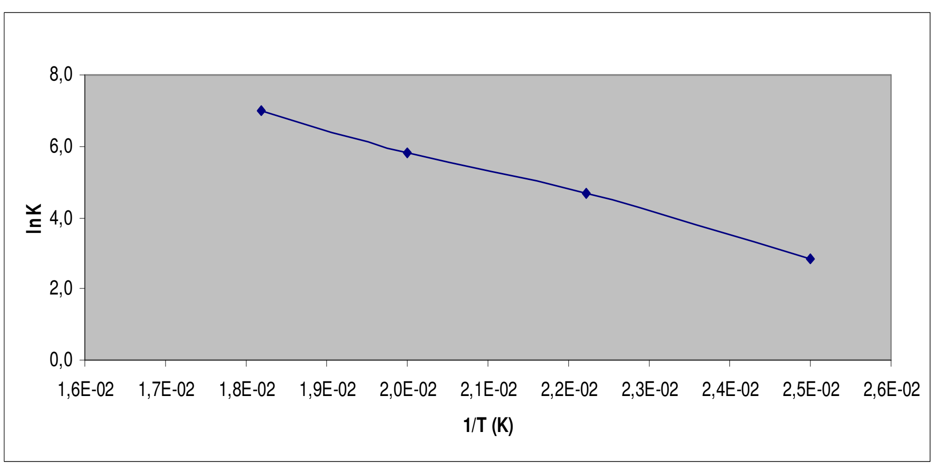

Figure B.3 : lnK=f(1/T) Curve $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) NaCl

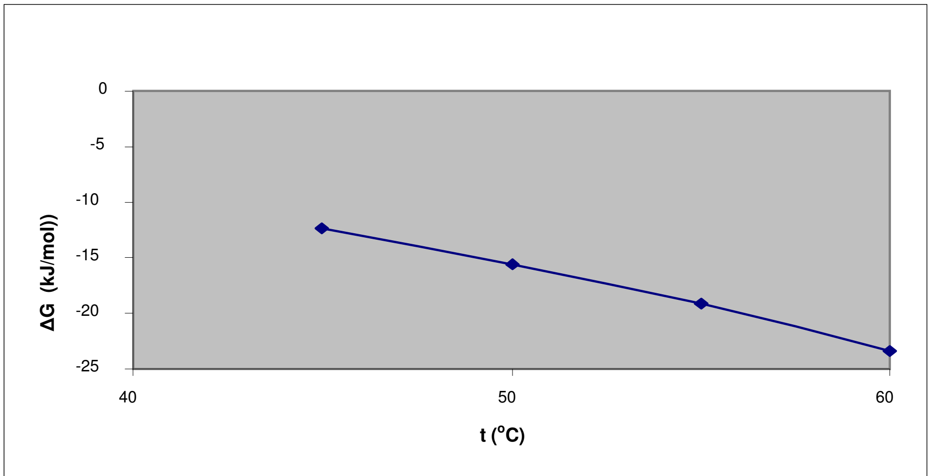

Figure B.4 : $\Delta G = f(t\ ^oC)$ curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) NaCl

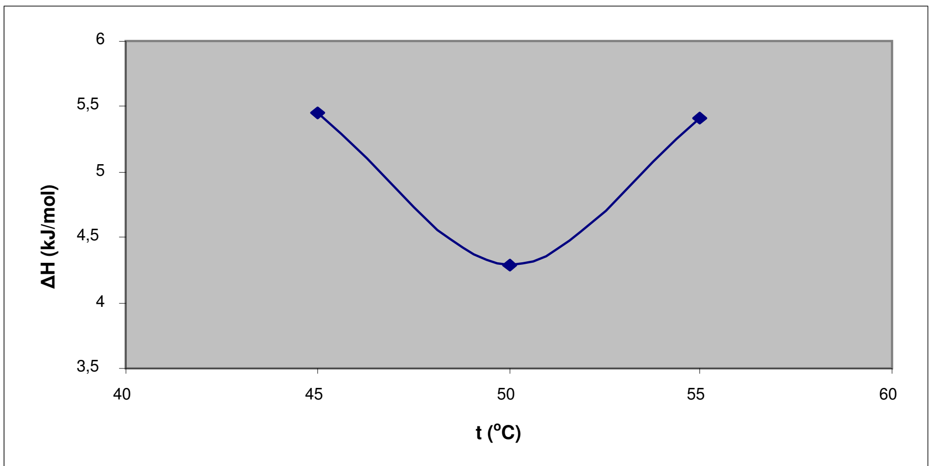

Figure B.5 : $\Delta H = f(t\ ^oC)$ curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) NaCl

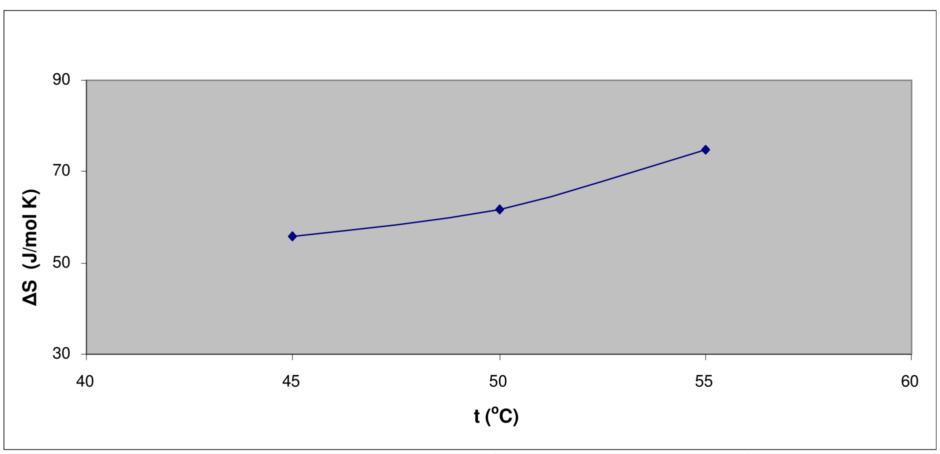

Figure B.6 : $\Delta S = f(t\ ^oC)$ curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) NaCl

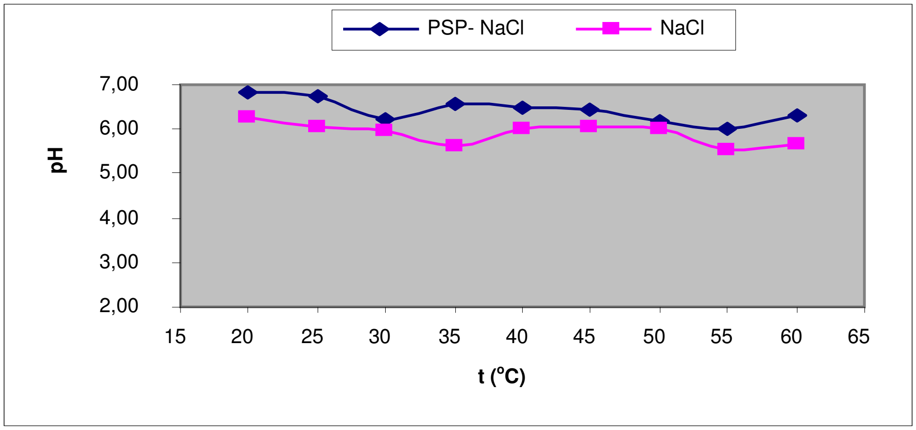

Figure B.7 : pH=f (t°C) curve of 1x10^{-2}(mo/L) PSP - 1x10^{-2}(mo/L) NaCl

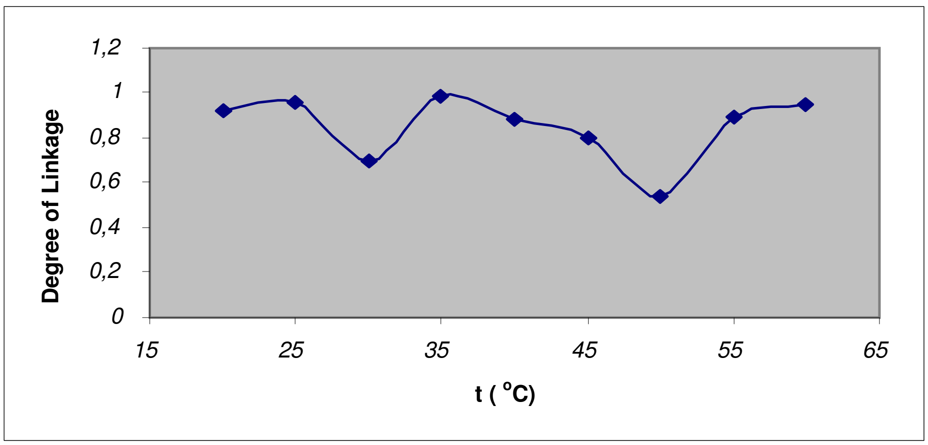

Figure B.8 : Degree of linkage, $\theta = f$ (t°C) Curve of 1x10^{-2}(mo/L) PSP – 1x10^{-2}(mo/L) NaCl

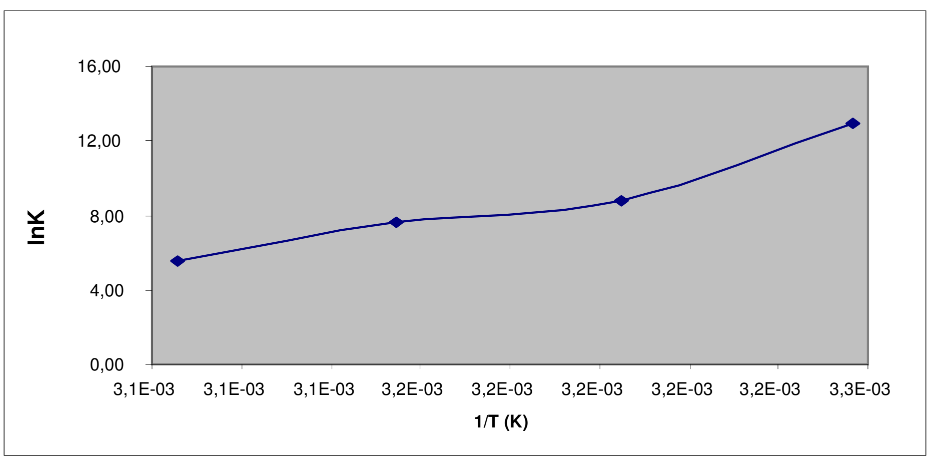

Figure B.9 : Curve of equilibrium constant 1x10^{-2}(mo/L) PSP – 1x10^{-2}(mo/L) NaCl

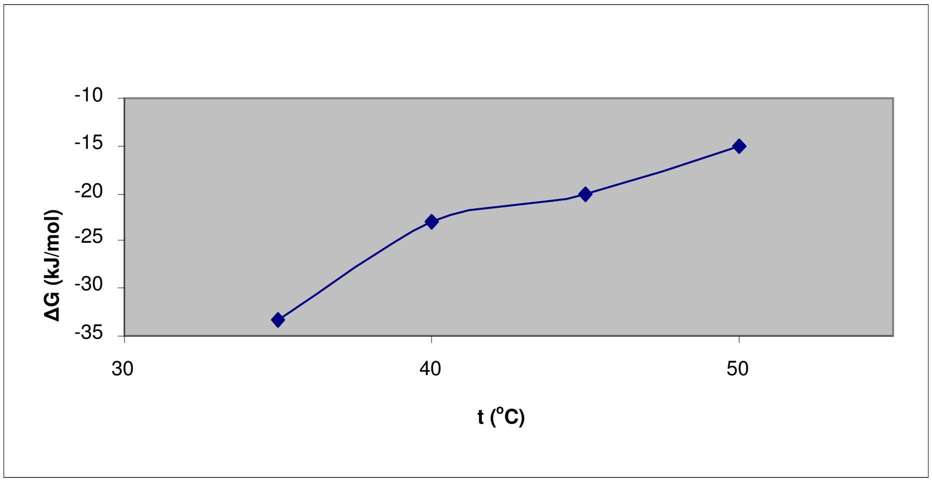

Figure B.10 : $\Delta G = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) NaCl

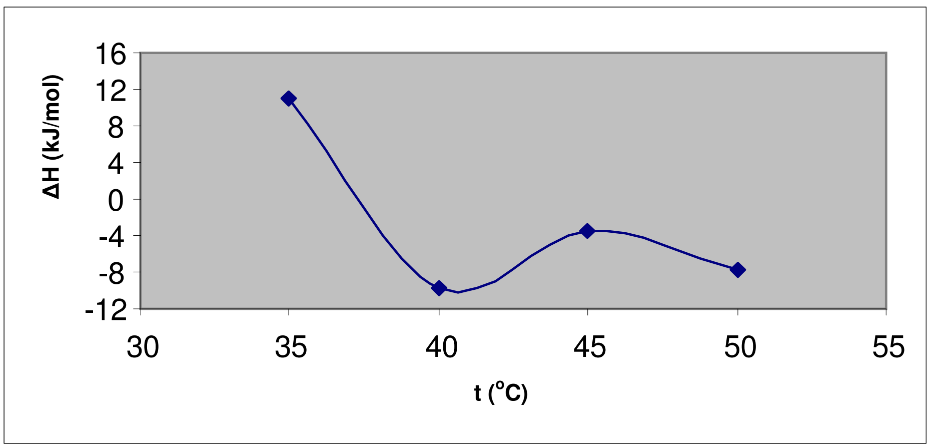

Figure B.11 : $\Delta H = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) NaCl

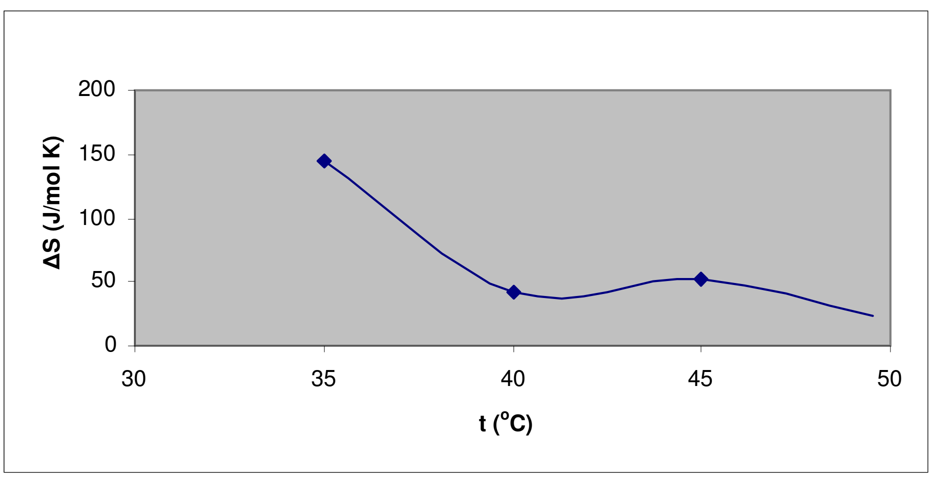

Figure B.12 : $\Delta S = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) NaCl

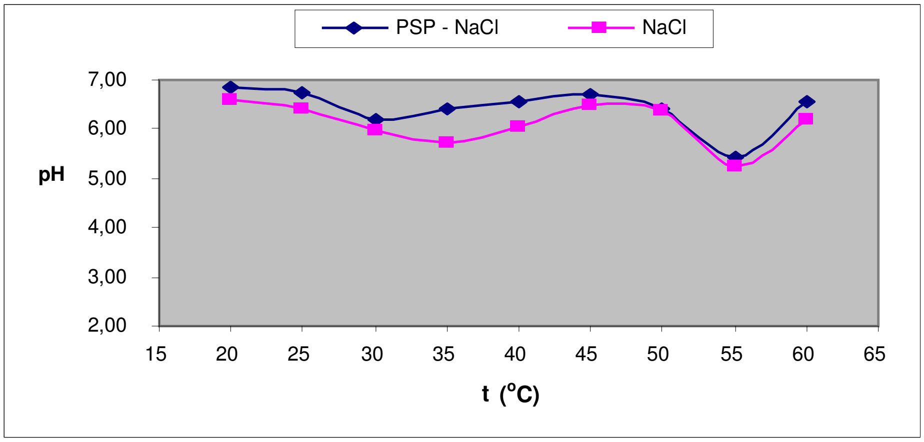

Figure B.13 : pH=f (t˚C) Curve of 1x10^{-3}(mo/L) PSP - 1x10^{-3}(mo/L) NaCl

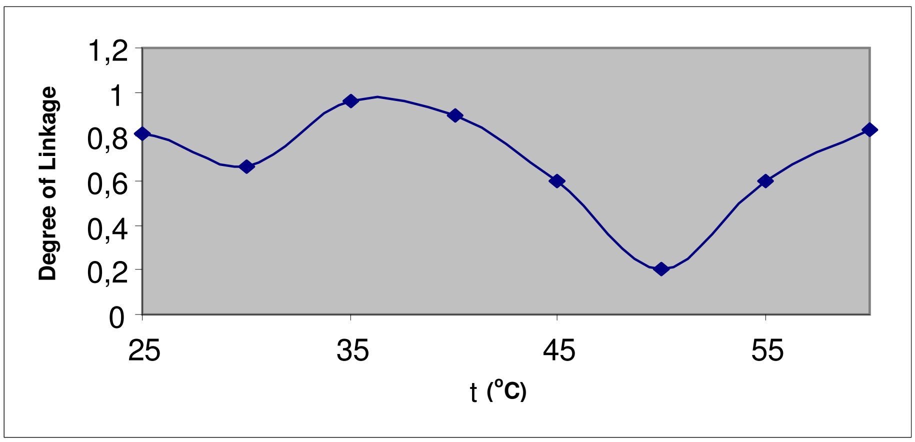

Figure B.14 : Degree of linkage, θ =f (t˚C) Curve of 1x10^{-3}(mo/L) PSP – 1x10^{-3}(mo/L) NaCl

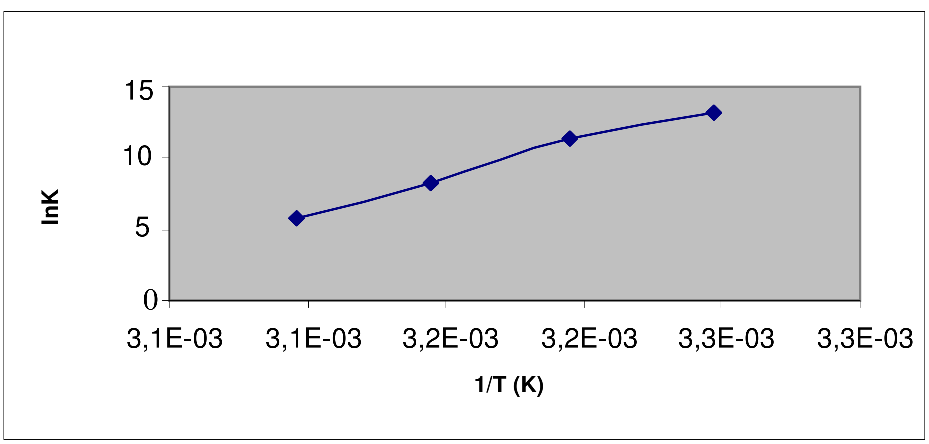

Figure B.15 : Curve of equilibrium constant 1x10^{-3}(mo/L) PSP – 1x10^{-3} (mo/L) NaCl

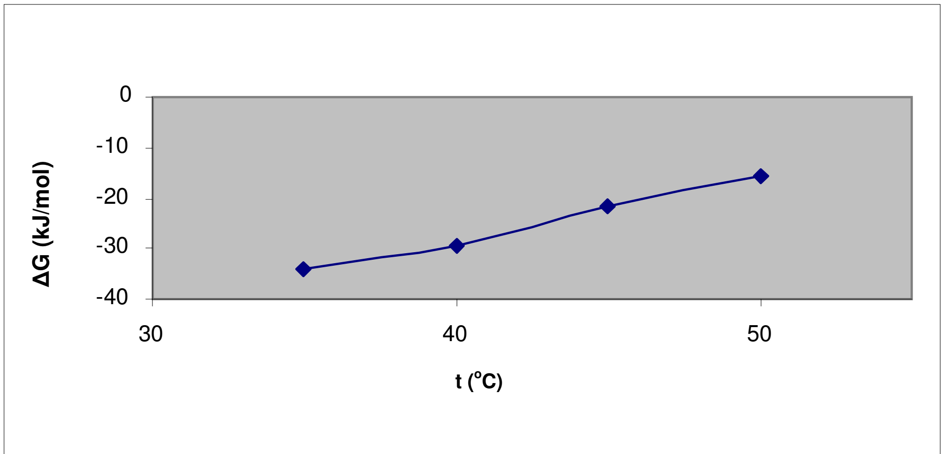

Figure B.16 : ΔG=*f* (t°C) Curve of 1x10^{-3}(mo/L) PSP - 1x10^{-3}(mo/L) NaCl

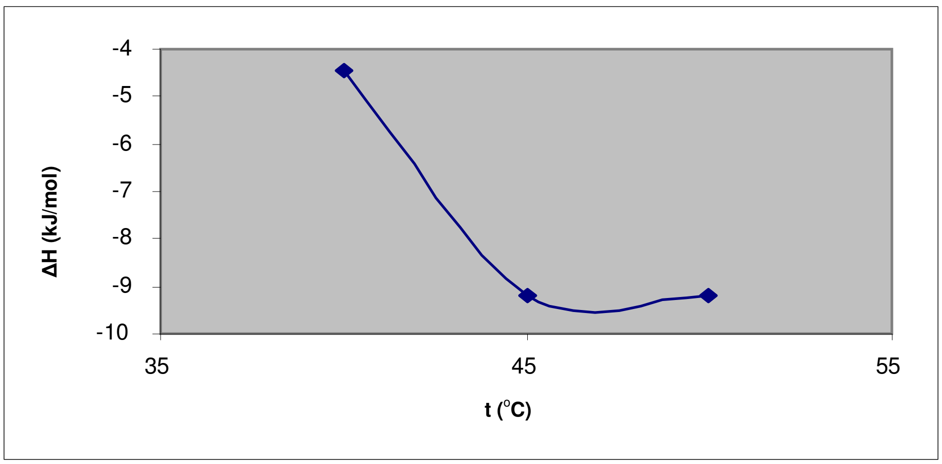

Figure B.17 : ΔH=*f* (t°C) Curve of 1x10^{-3}(mo/L) PSP - 1x10^{-3}(mo/L) NaCl

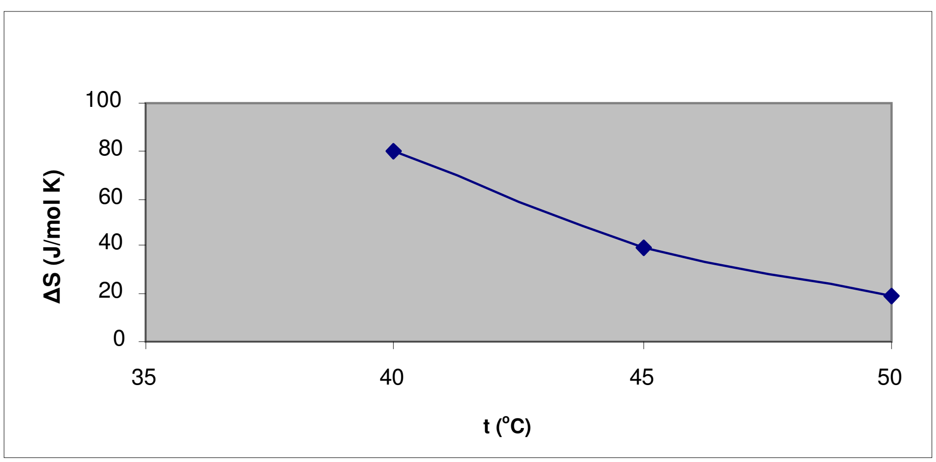

Figure B.18 : ΔS=*f* (t°C) Curve of 1x10^{-3}(mo/L) PSP - 1x10^{-3}(mo/L) NaCl

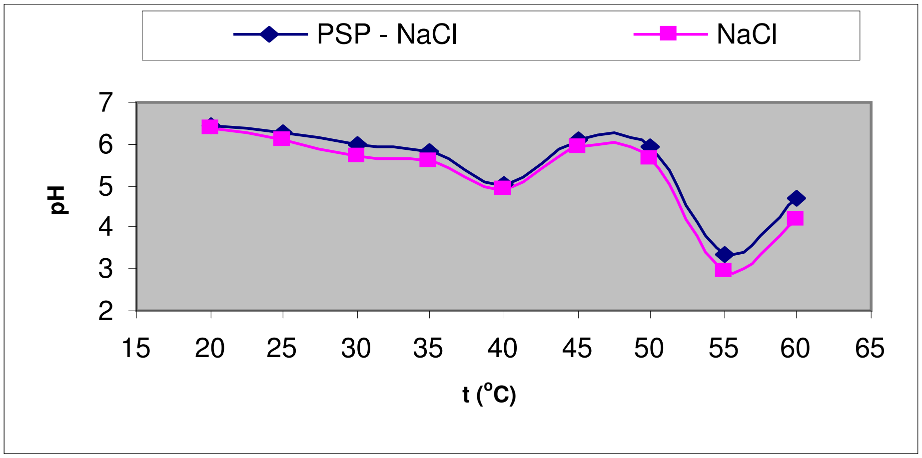

Figure B.19 : pH=f (t°C) curve of 1x10^{-4}(mo/L) PSP - 1x10^{-4}(mo/L) NaCl

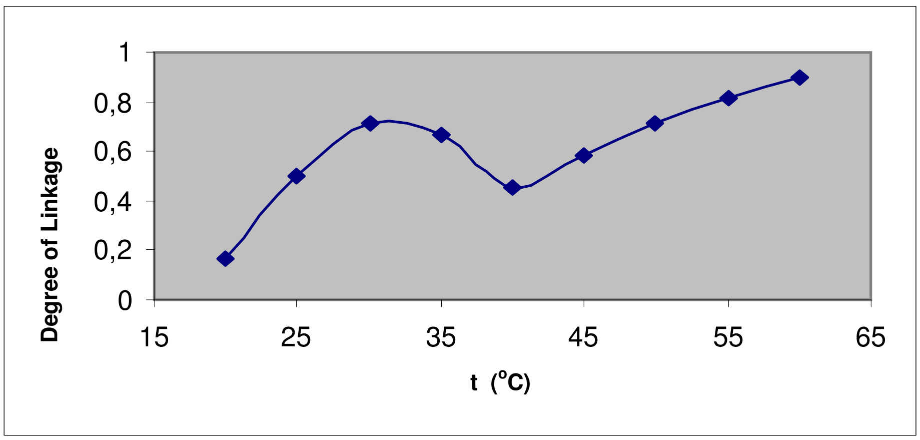

Figure B.20 : Degree of linkage, $\theta = f$ (t°C) Curve of 1x10^{-4}(mo/L) PSP – 1x10^{-4}(mo/L) NaCl

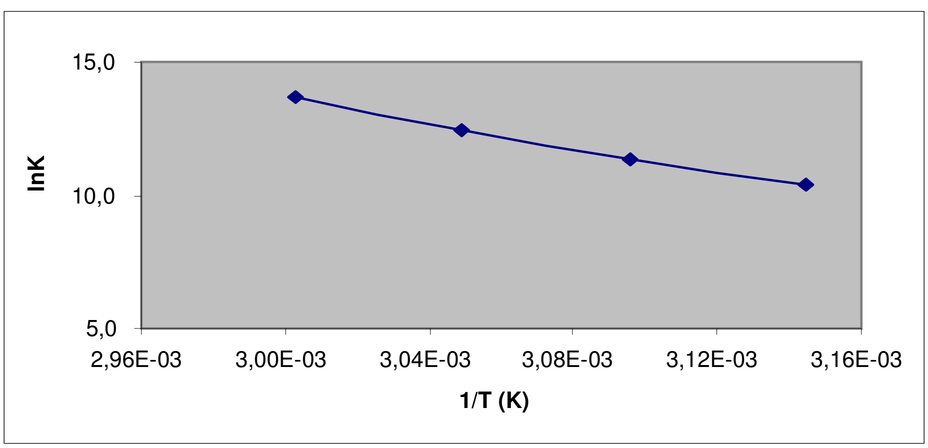

Figure B.21 : Curve of equilibrium constant 1x10^{-4}(mo/L) PSP – 1x10^{-4} (mo/L) NaCl

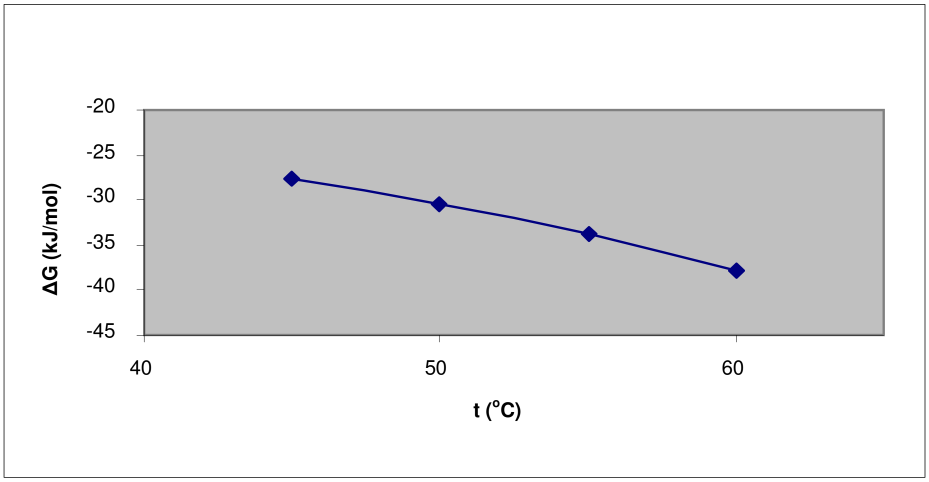

Figure B.22 : $\Delta G = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

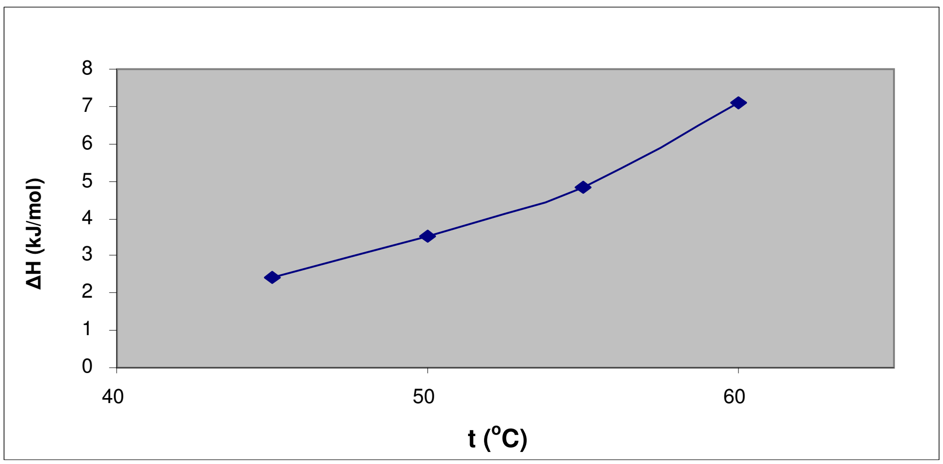

Figure B.23 : $\Delta H = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

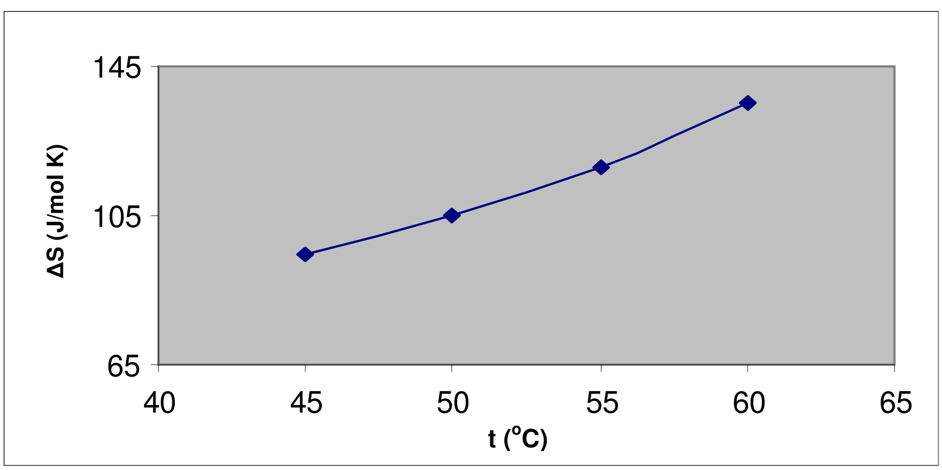

Figure B.24 : $\Delta S = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) NaCl

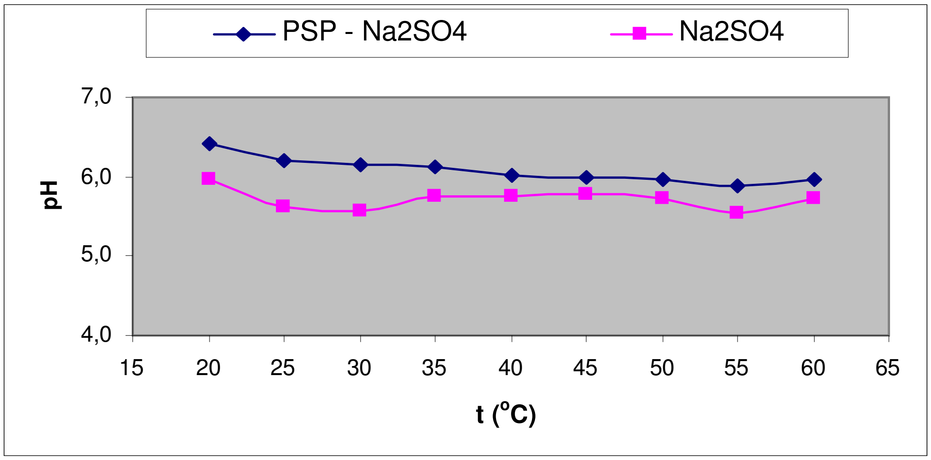

Figure B.25 : pH=f (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) Na_2SO_4

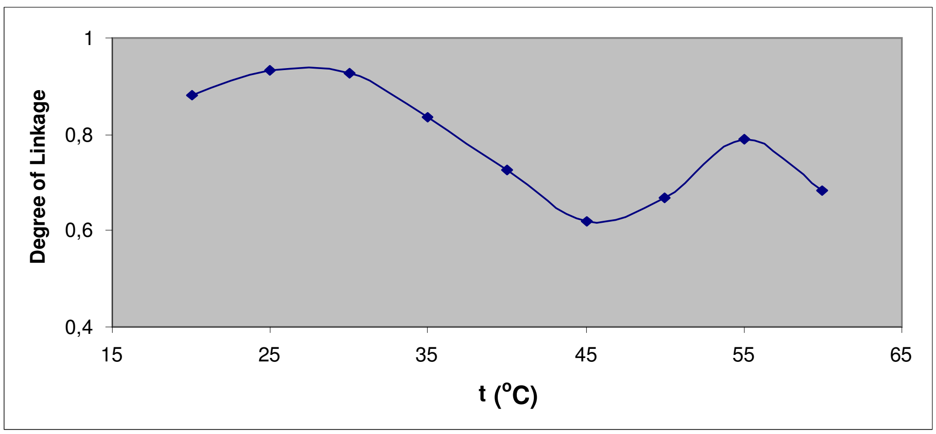

Figure B.26 : Degree of linkage, $\theta = f$ (t˚C) Curve of $1x10^{-1}$(mo/L) PSP – $1x10^{-1}$(mo/L) Na_2SO_4

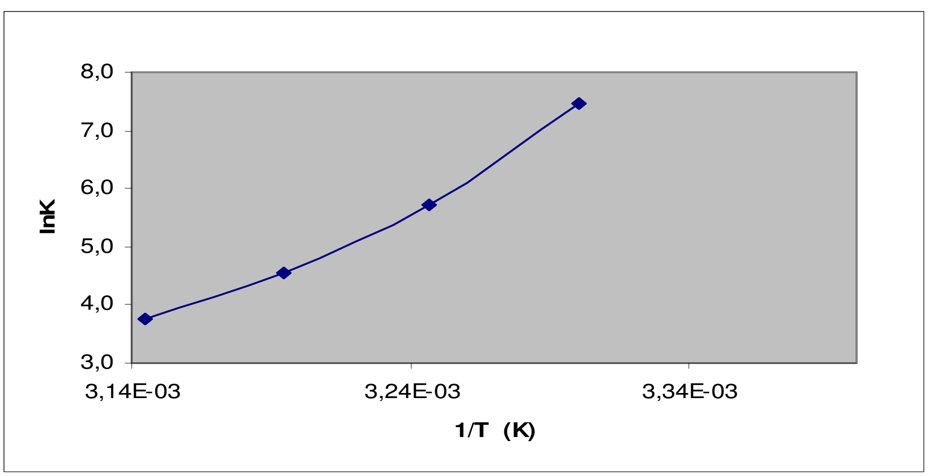

Figure B.27 : Curve of equilibrium constant $1x10^{-1}$(mo/L) PSP – $1x10^{-1}$ (mo/L) Na_2SO_4

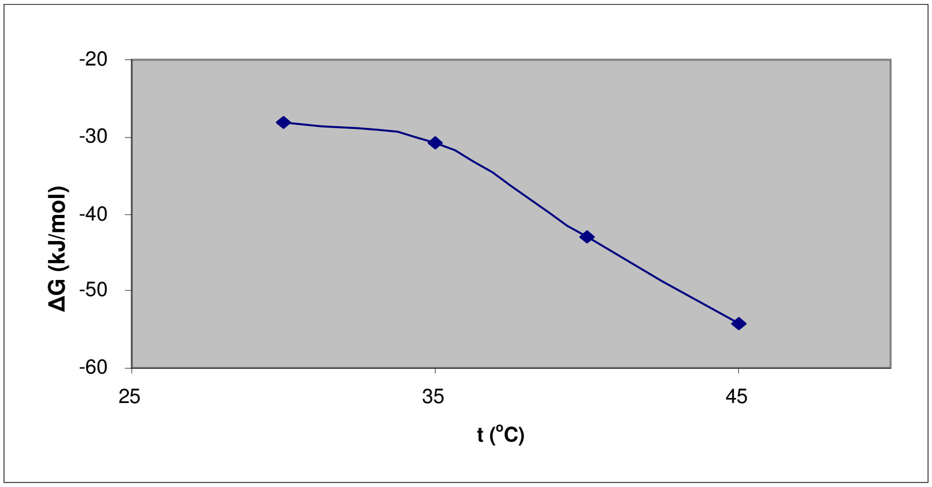

Figure B.28 : ΔG=f (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) Na_2SO_4

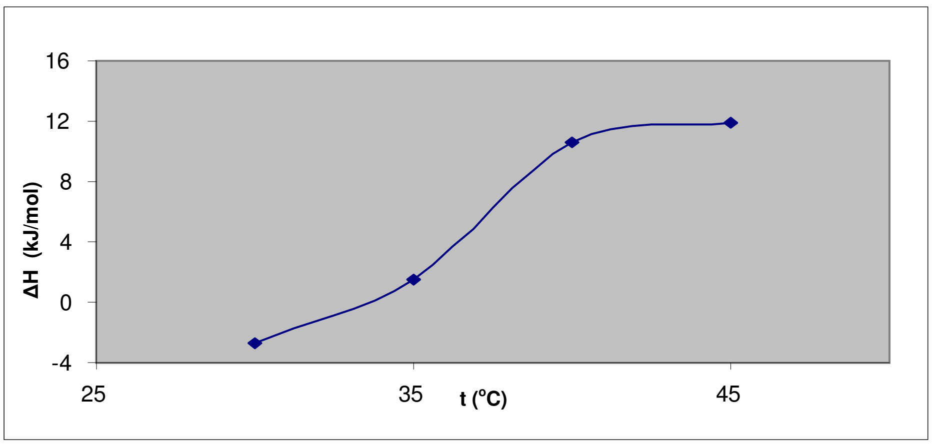

Figure B.29: ΔH=f (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) Na_2SO_4

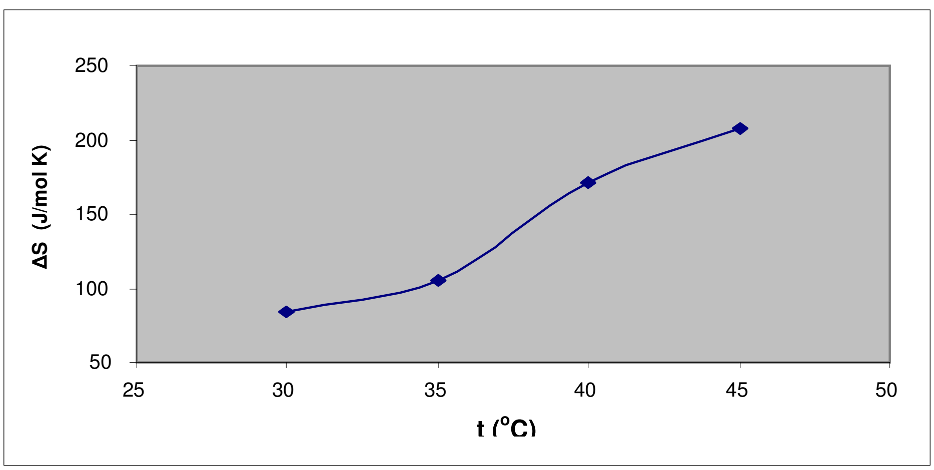

Figure B.29 : ΔS=f (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) Na_2SO_4

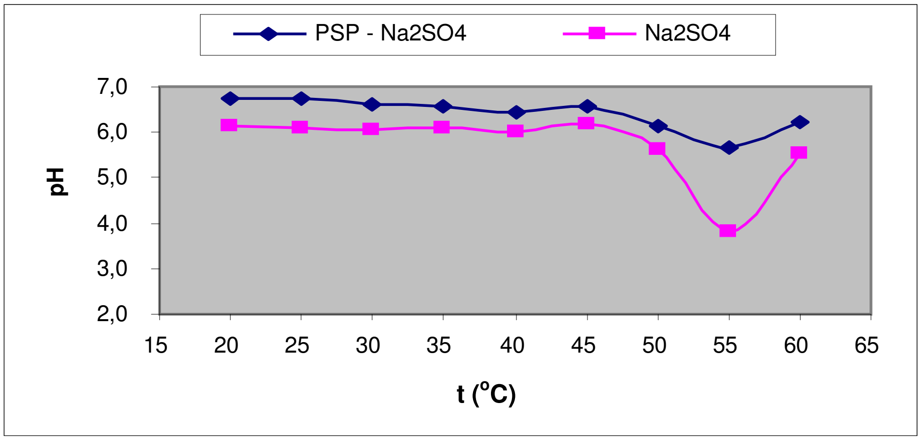

Figure B.30 : pH=f (t°C) curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) Na_2SO_4

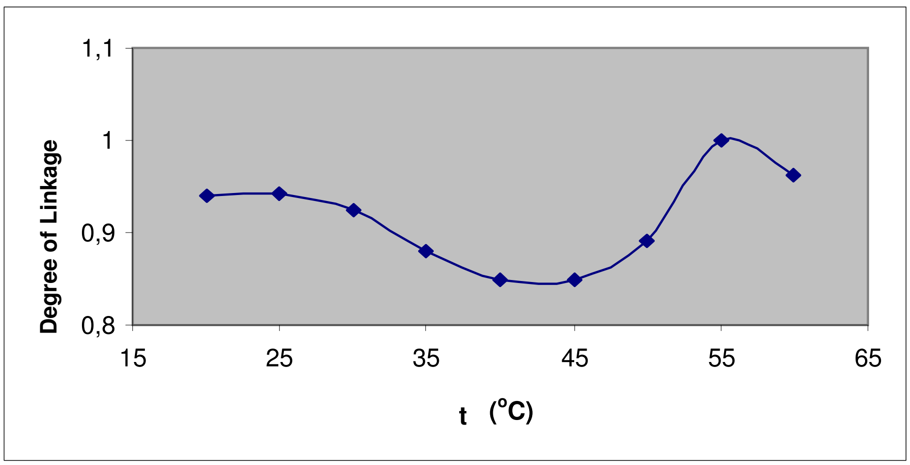

Figure B.31 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP – $1x10^{-2}$(mo/L)Na_2SO_4

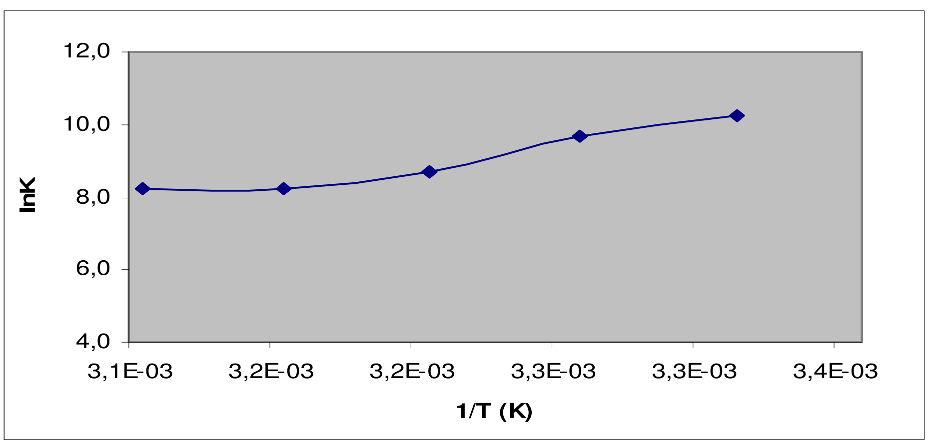

Figure B.32 : Curve of equilibrium constant $1x10^{-2}$(mo/L) PSP – $1x10^{-2}$ (mo/L) Na_2SO_4

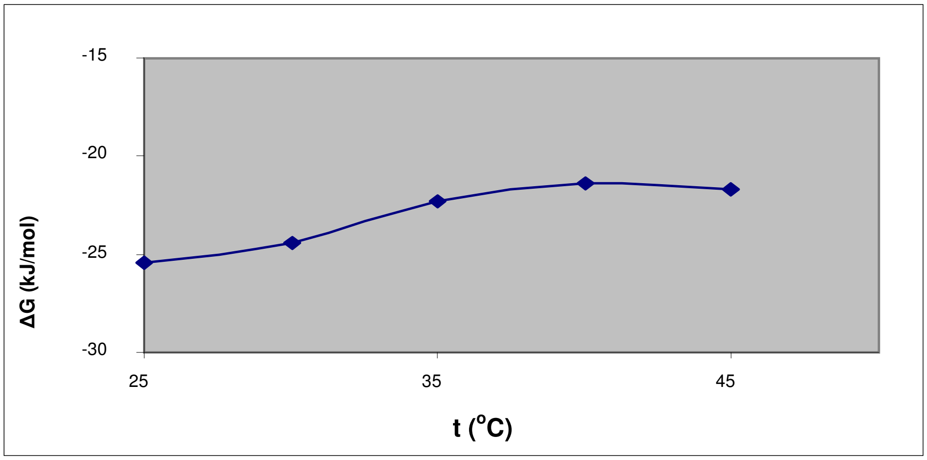

Figure B.33 : $\Delta G = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) Na_2SO_4

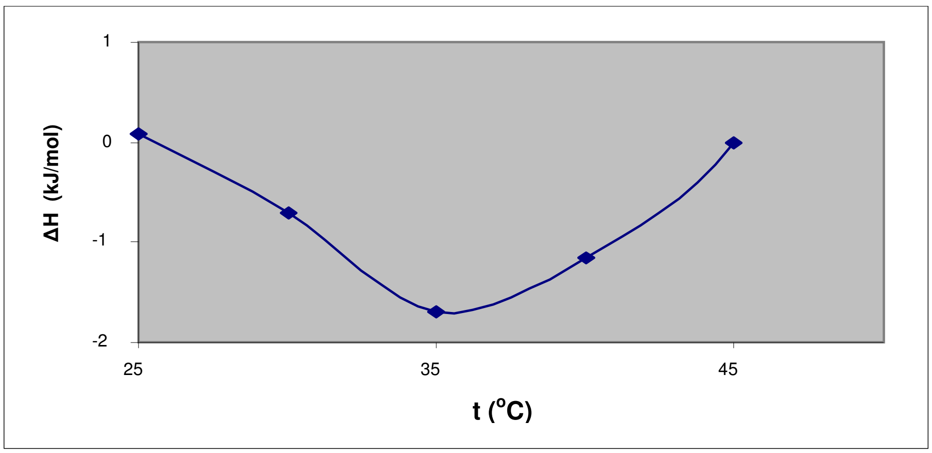

Figure B.34 : $\Delta H = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) Na_2SO_4

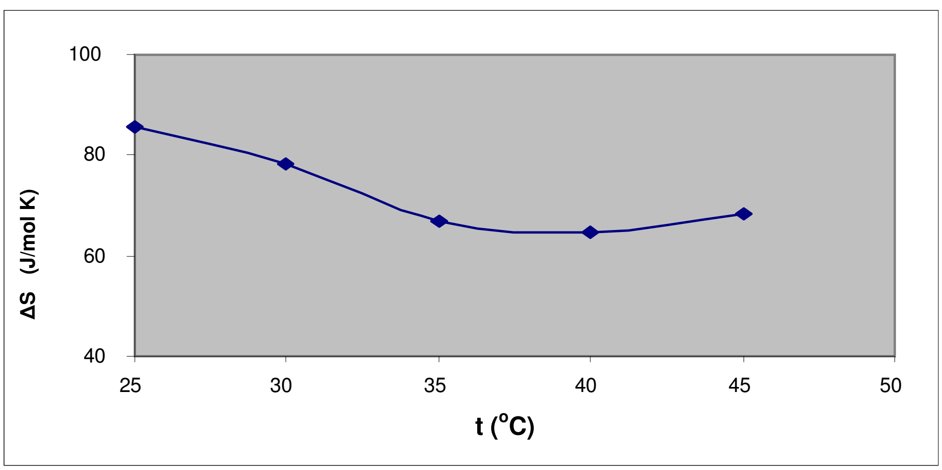

Figure B.35 : $\Delta S = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) Na_2SO_4

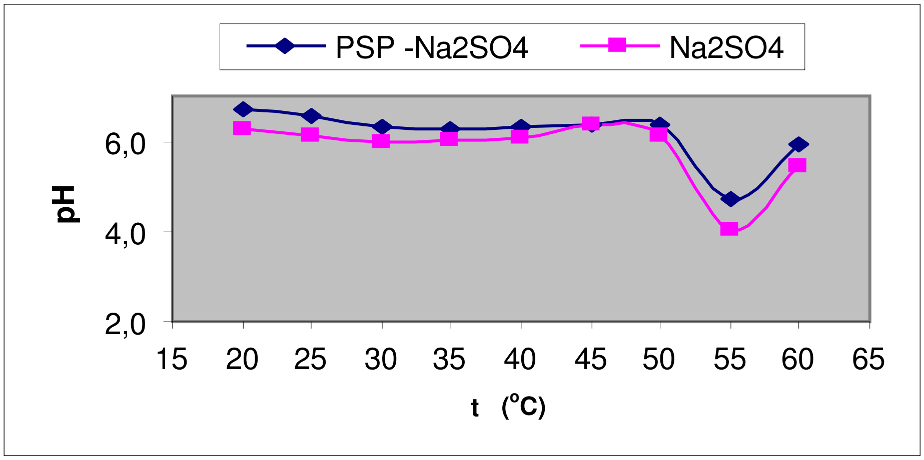

Figure B.36 : pH=f (t°C) Curve of of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) Na_2SO_4

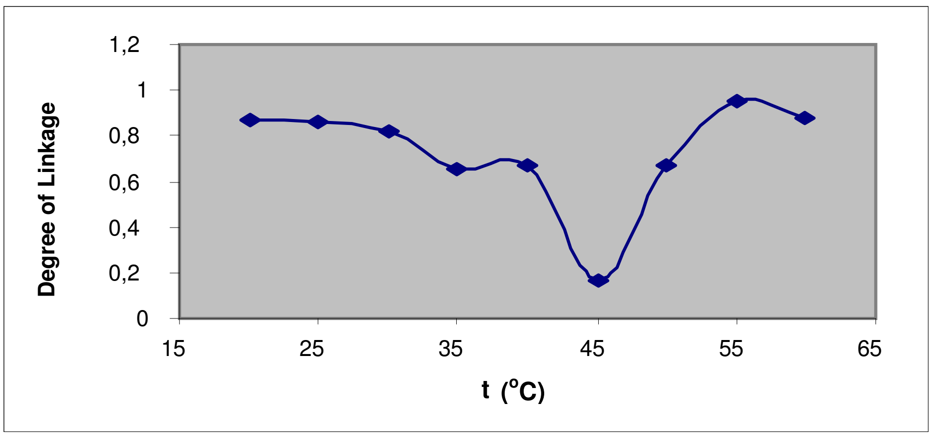

Figure B.37 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-3}$(mo/L) PSP – $1x10^{-3}$(mo/L) Na_2SO_4

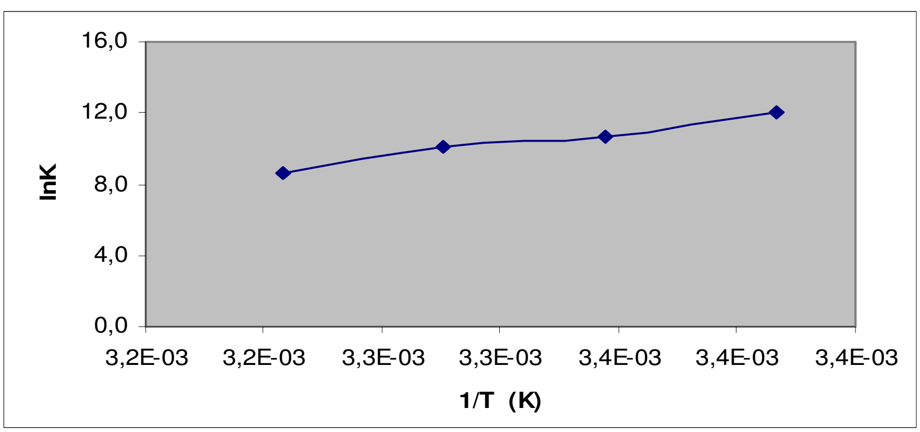

Figure B.38 : Curve of equilibrium constant $1x10^{-3}$(mo/L) PSP – $1x10^{-3}$ (mo/L) Na_2SO_4

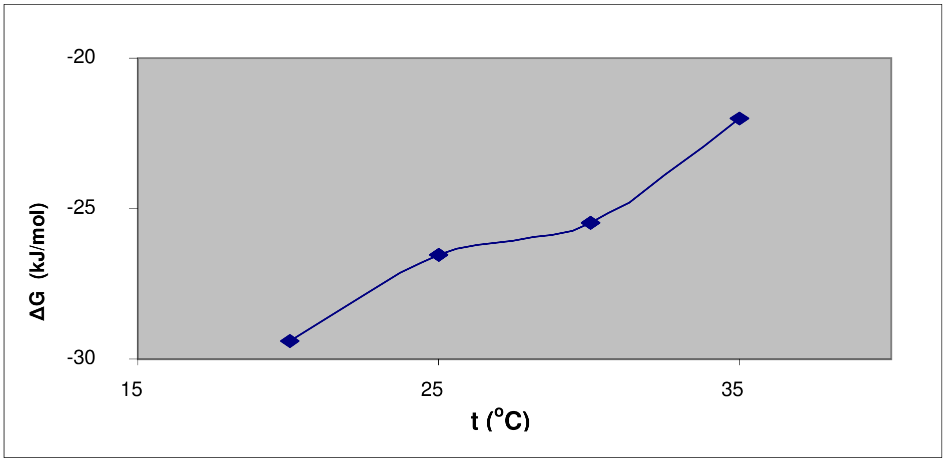

Figure B.39 : $\Delta G = f$ (t˚C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) Na_2SO_4

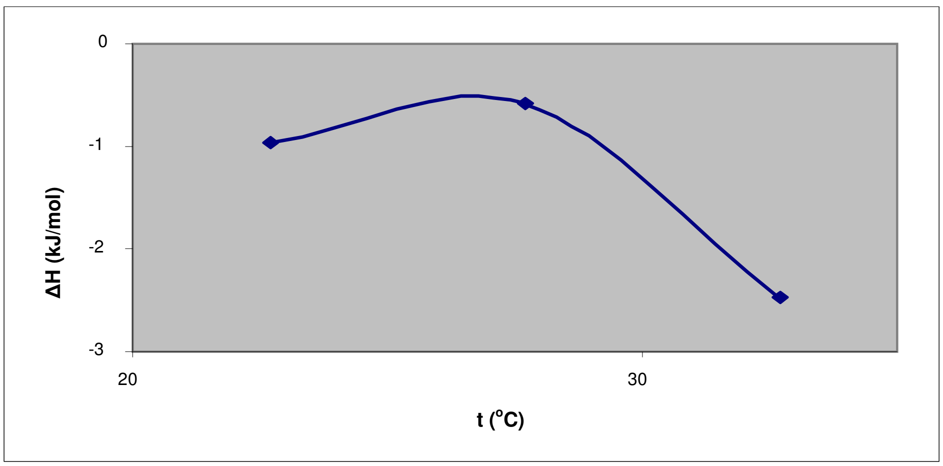

Figure B.40 : $\Delta H = f$ (t˚C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) Na_2SO_4

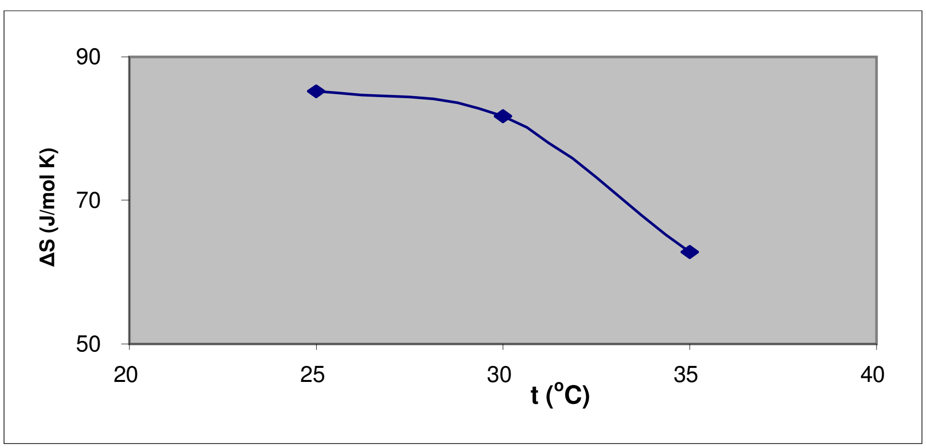

Figure B.41 : $\Delta S = f$ (t˚C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) Na_2SO_4

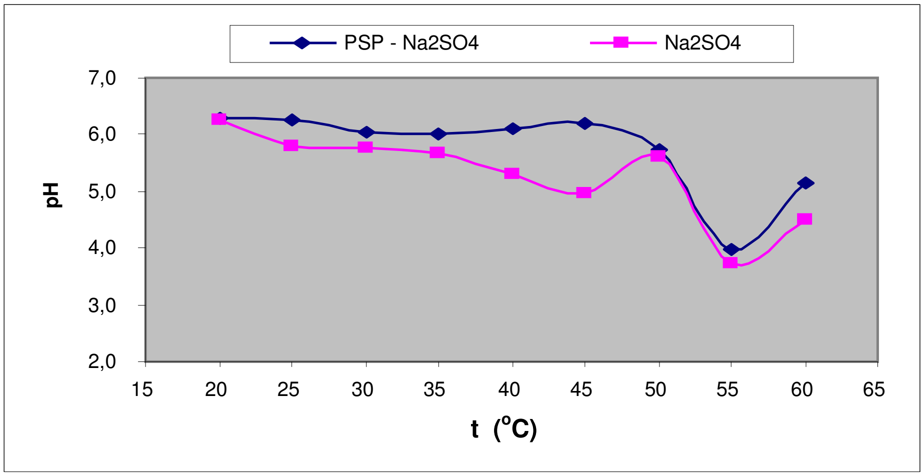

Figure B.42 : pH=*f* (t°C) curve of of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) Na_2SO_4

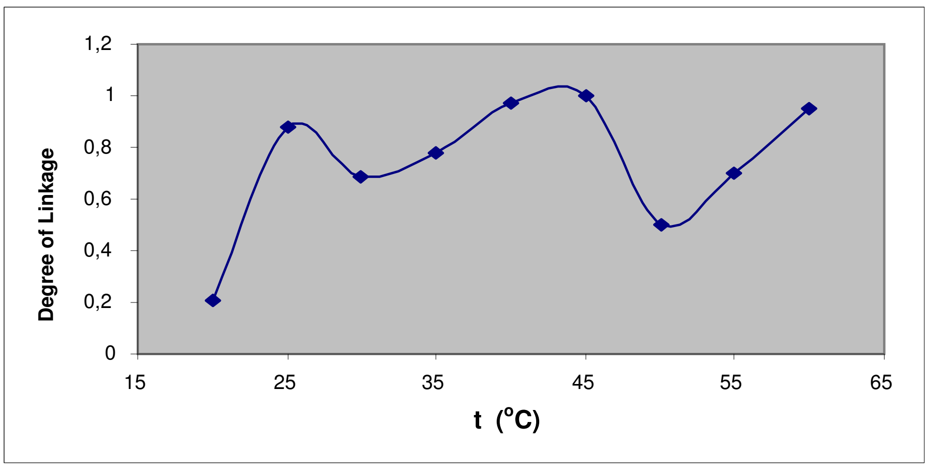

Figure B.43 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-4}$(mo/L) PSP – $1x10^{-4}$(mo/L) Na_2SO_4

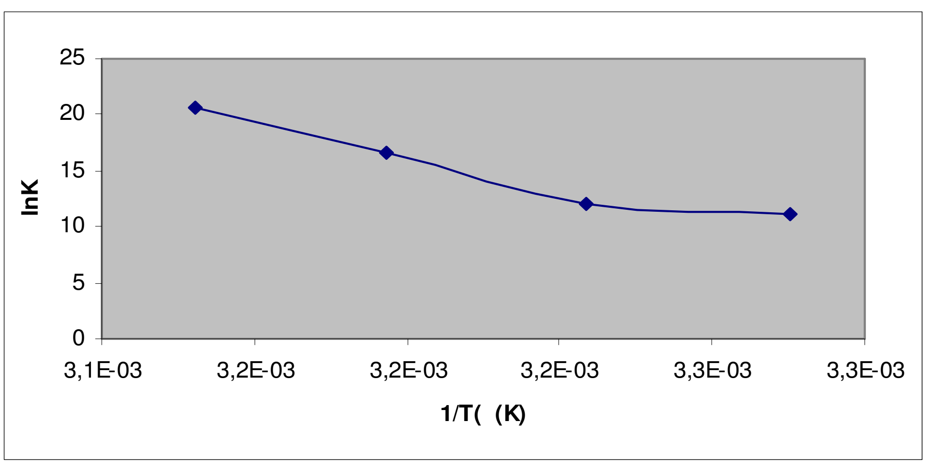

Figure B.44 : Curve of equilibrium constant $1x10^{-4}$(mo/L) PSP – $1x10^{-4}$ (mo/L) Na_2SO_4

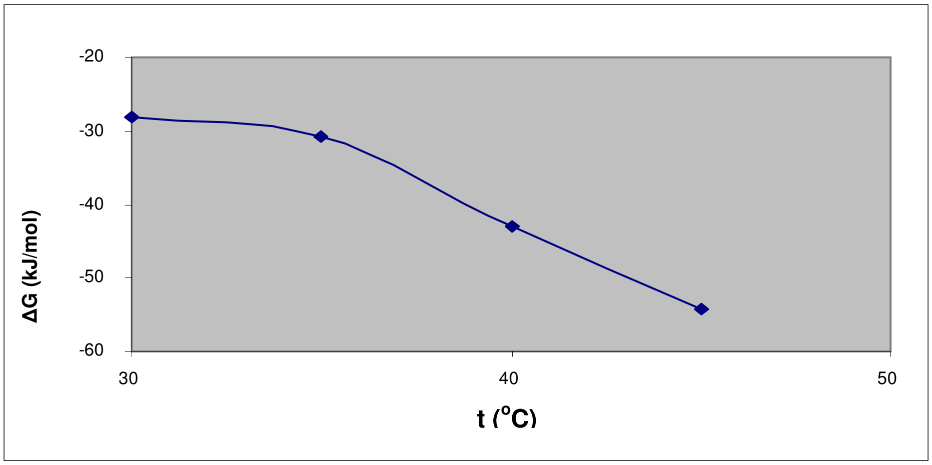

Figure B.45 : $\Delta G = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) Na_2SO_4

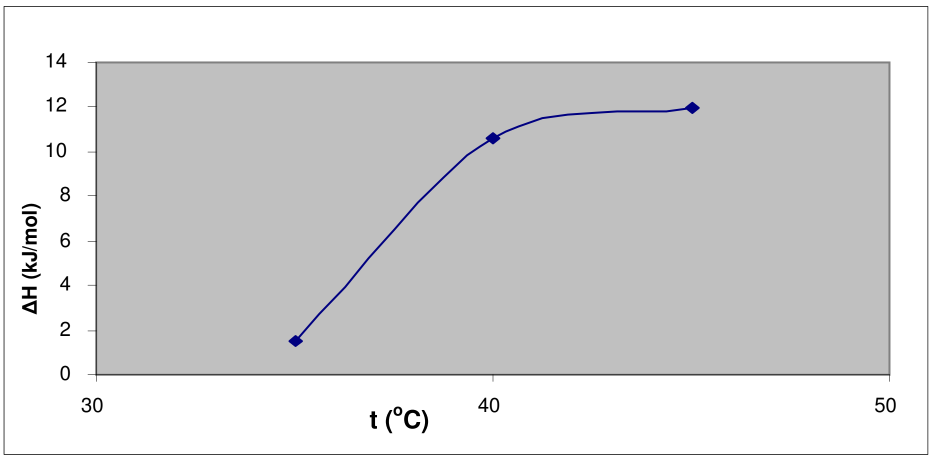

Figure B.46 : $\Delta H = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) Na_2SO_4

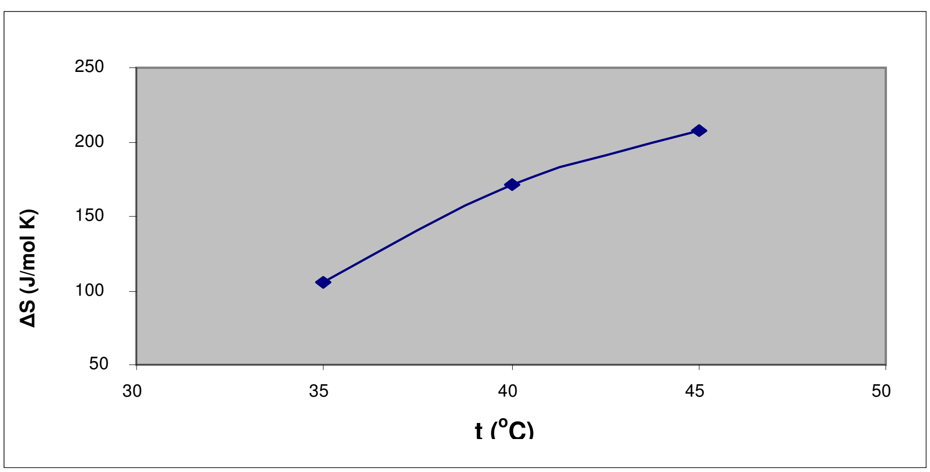

Figure B.47 : $\Delta S = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) Na_2SO_4

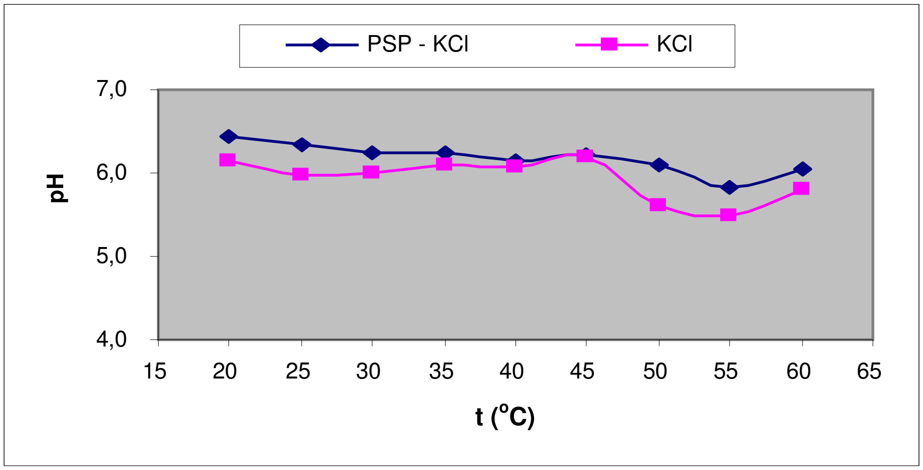

Figure B.48 : pH=f (t°C) curve of of 1x10^{-1}(mo/L) PSP - 1x10^{-1}(mo/L) KCl

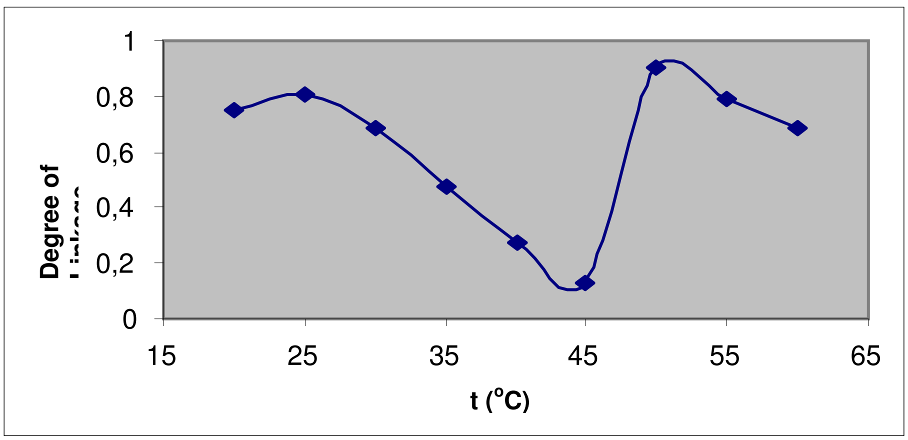

Figure B.49 : Degree of linkage, θ =f (t°C) Curve of 1x10^{-1}(mo/L) PSP – 1x10^{-1}(mo/L) KCl

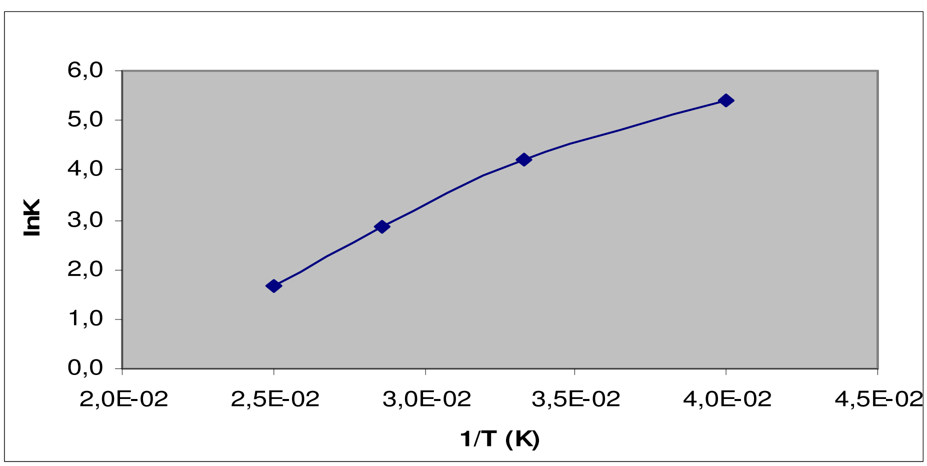

Figure B.50 : Curve of equilibrium constant 1x10^{-1}(mo/L) PSP – 1x10^{-1} (mo/L) KCl

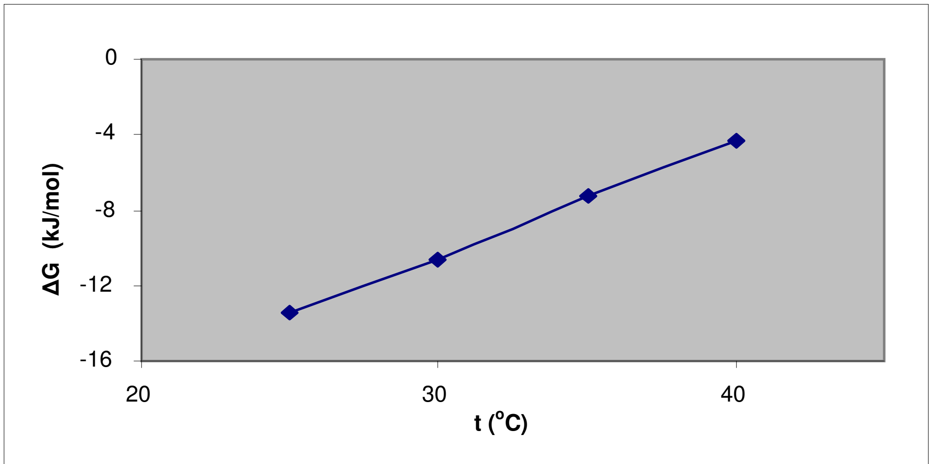

Figure B.51 : ΔG=*f* (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L)KCl

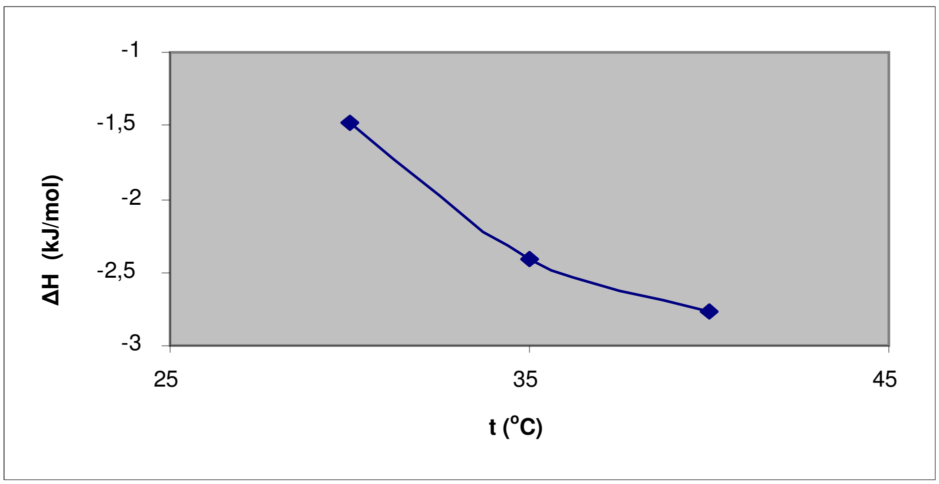

Figure B.52 : ΔH=*f* (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) KCl

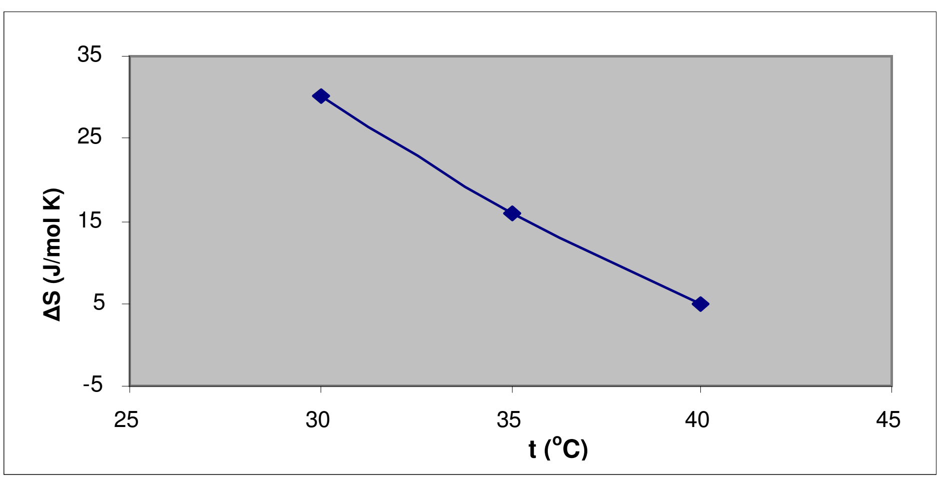

Figure B.53 : ΔS=*f* (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) KCl

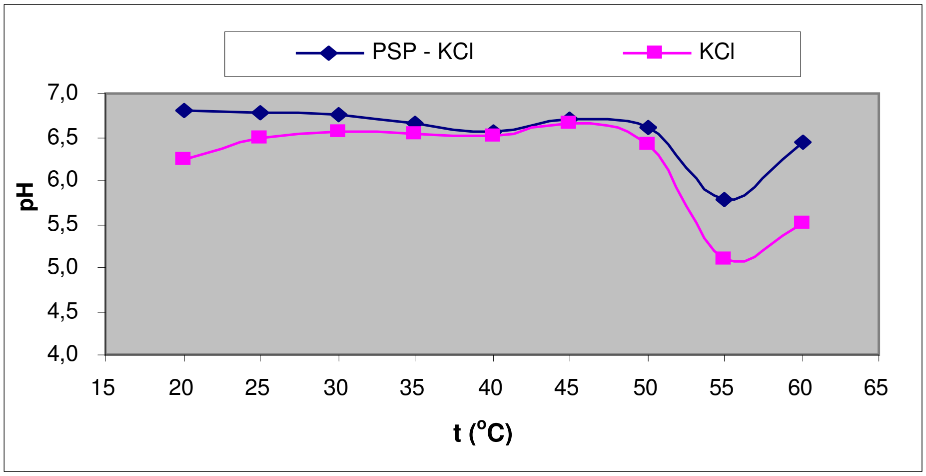

Figure B.54 : pH= f (t˚C) Curve of of 1x10^{-2}(mo/L) PSP - 1x10^{-2}(mo/L) KCl

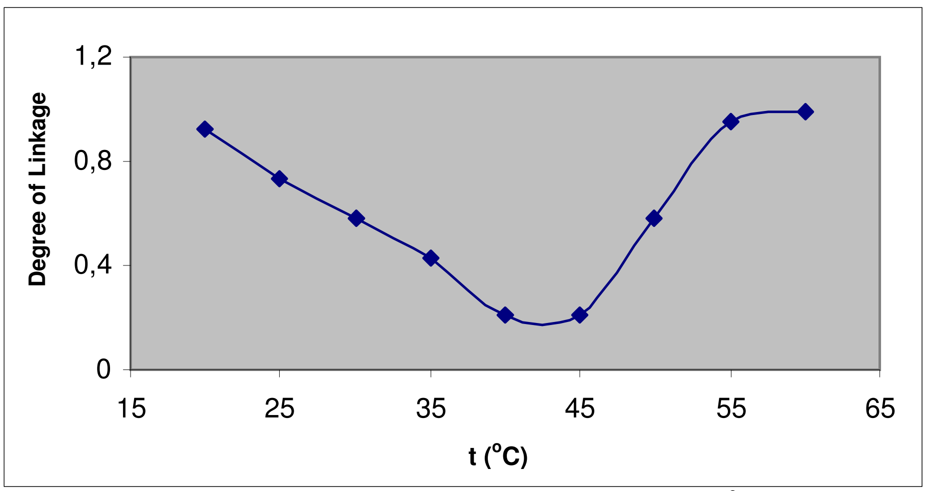

Figure B.55 : Degree of linkage, θ = f (t˚C) Curve of 1x10^{-2}(mo/L) PSP – 1x10^{-2}(mo/L) KCl

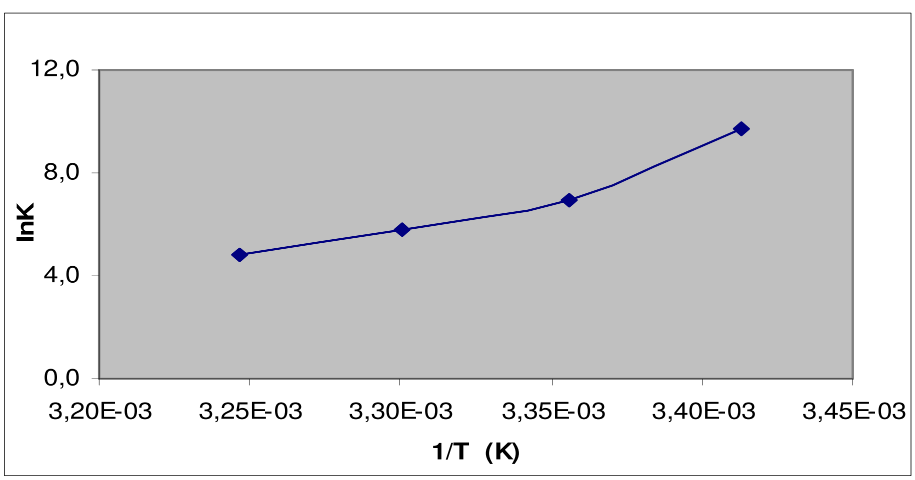

Figure B.56 : Curve of equilibrium constant 1x10^{-2}(mo/L) PSP – 1x10^{-2} (mo/L) KCl

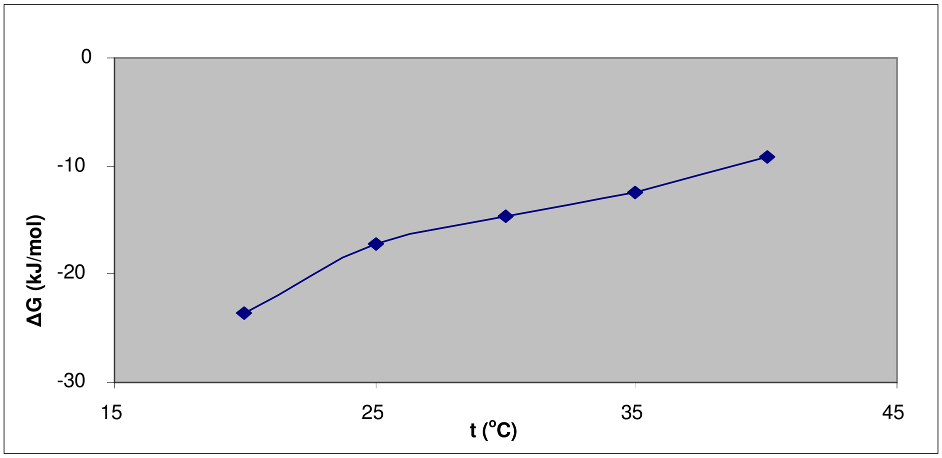

Figure B.57 : ΔG=f (t°C) Curve of 1x10^{-2}(mo/L) PSP - 1x10^{-2}(mo/L) KCl

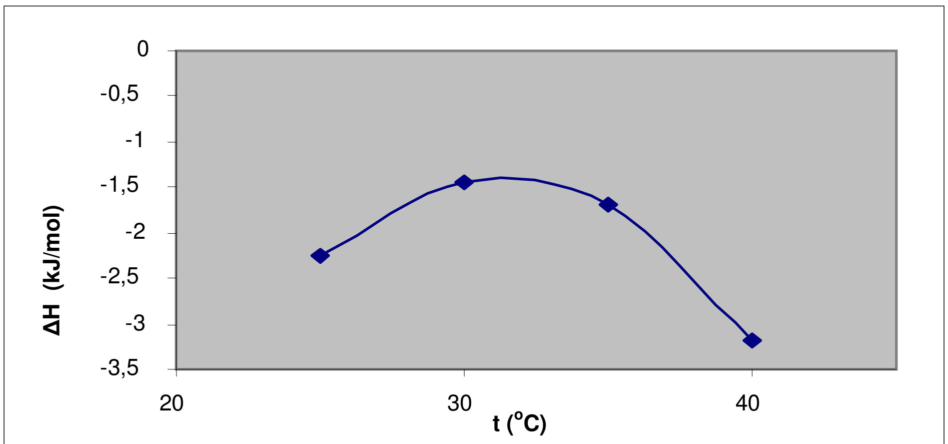

Figure B.58 : ΔH=f (t°C) Curve of 1x10^{-2}(mo/L) PSP - 1x10^{-2}(mo/L) KCl

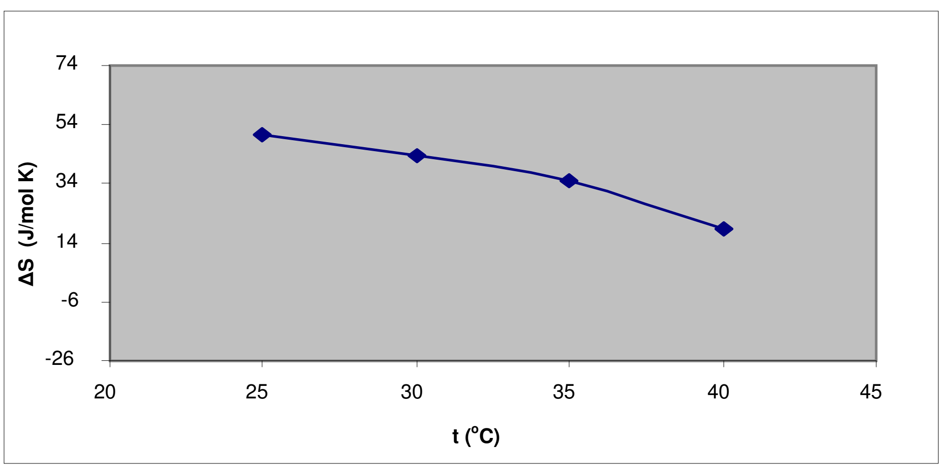

Figure B.59 : ΔS=f (t°C) Curve of 1x10^{-2}(mo/L) PSP - 1x10^{-2}(mo/L) KCl

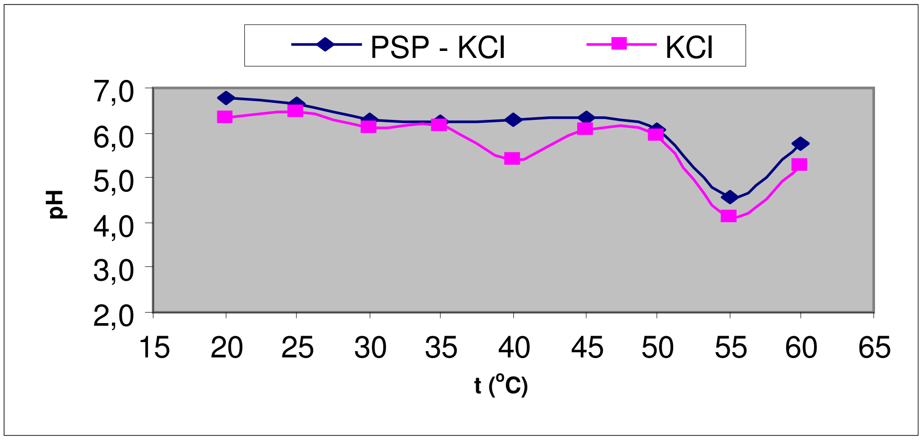

Figure B.60 : pH=f (t˚C) curve of of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) KCl

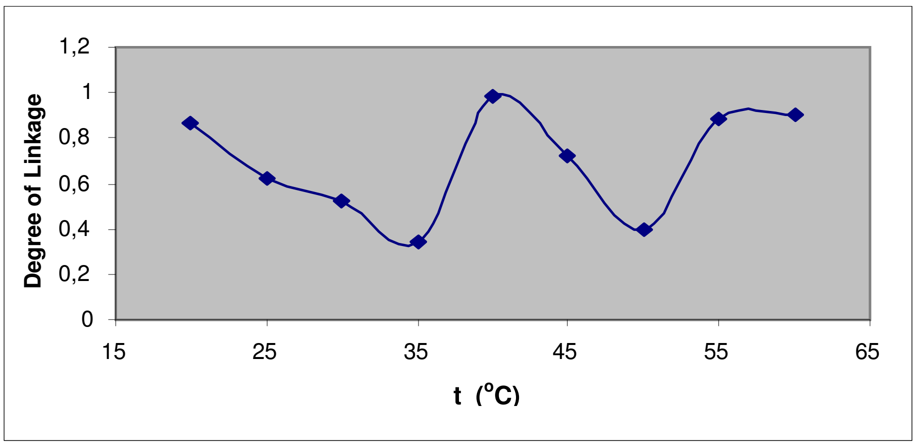

Figure B.61 : Degree of linkage, θ =f (t˚C) Curve of $1x10^{-3}$(mo/L) PSP – $1x10^{-3}$(mo/L) KCl

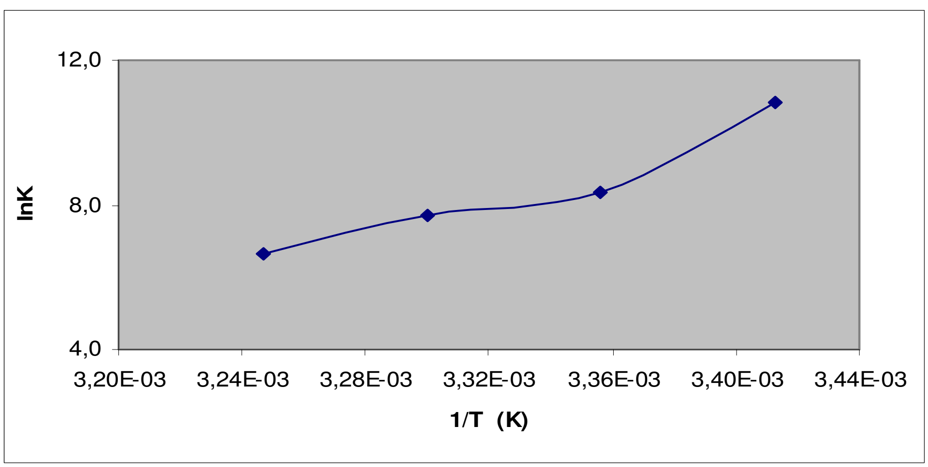

Figure B.62 : Curve of equilibrium constant $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$ (mo/L) KCl

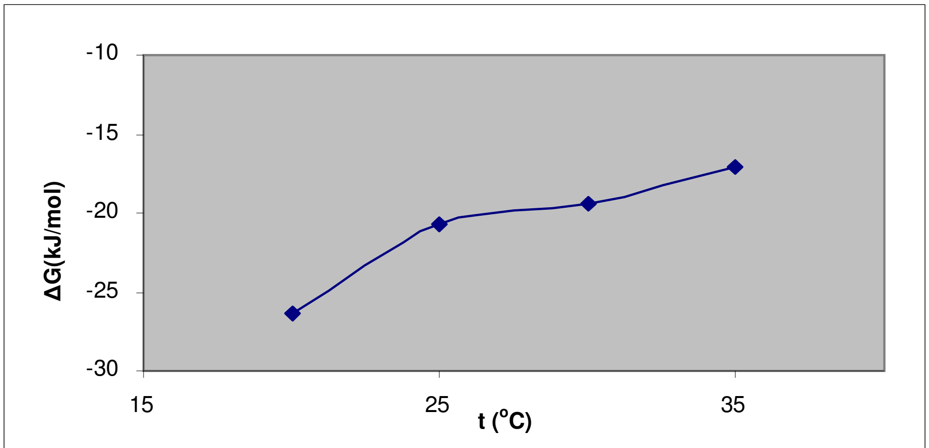

Figure B.63 : $\Delta G = f\,(t°C)$ Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) KCl

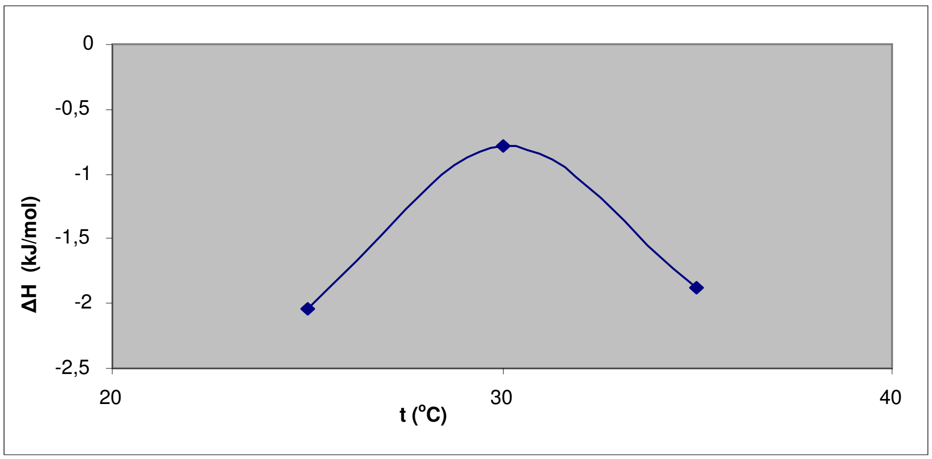

Figure B.64 : $\Delta H = f\,(t°C)$ Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) KCl

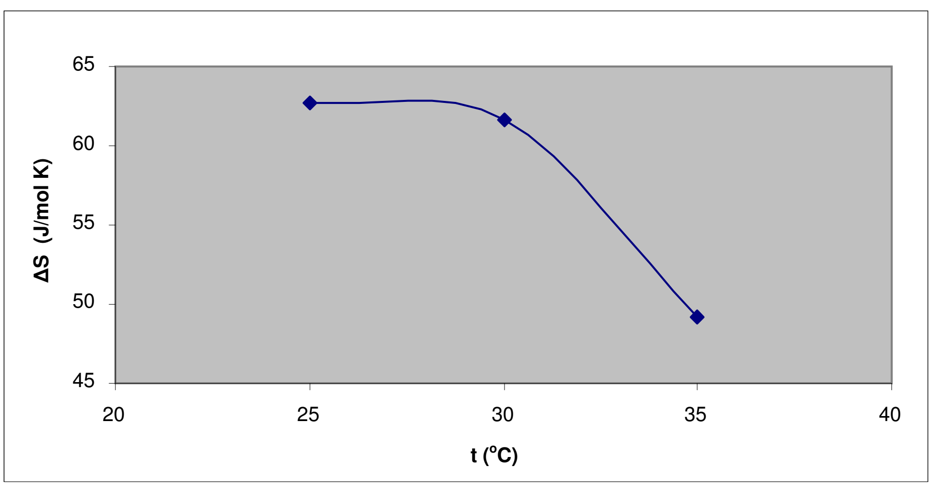

Figure B.65 : $\Delta S = f\,(t°C)$ Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) KCl

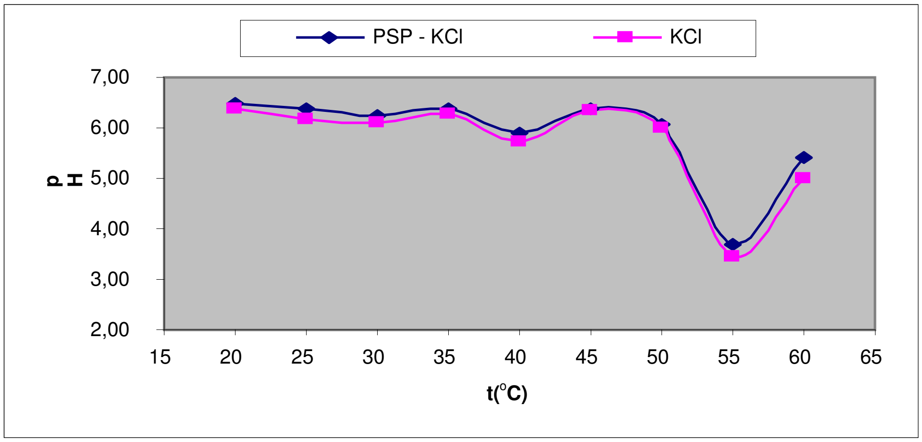

Figure B.66 : pH=*f* (t˚C) curve of of 1x10^{-4}(mo/L) PSP - 1x10^{-4}(mo/L) KCl

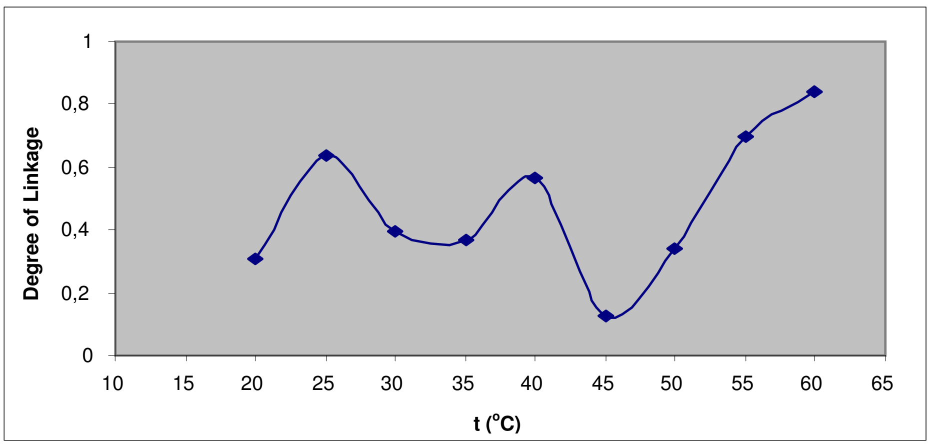

Figure B.67 : Degree of linkage, θ =*f* (t˚C) Curve of 1x10^{-4}(mo/L) PSP – 1x10^{-4} (mo/L) KCl

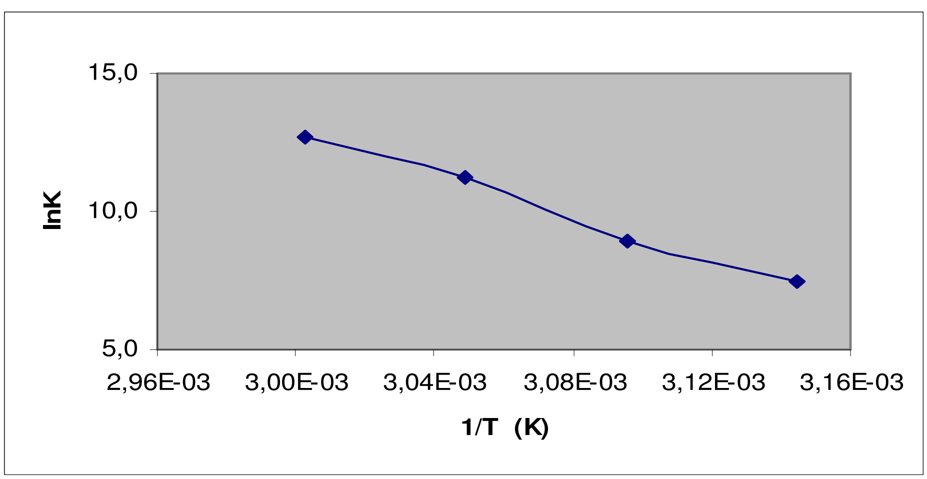

Figure B.68 : Curve of equilibrium constant 1x10^{-4}(mo/L) PSP – 1x10^{-4} (mo/L) KCl

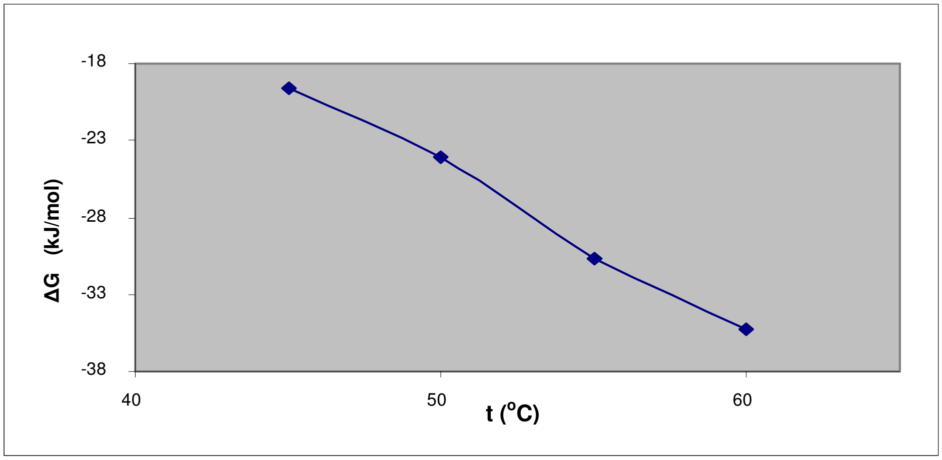

Figure B.69 : $\Delta G = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) KCl

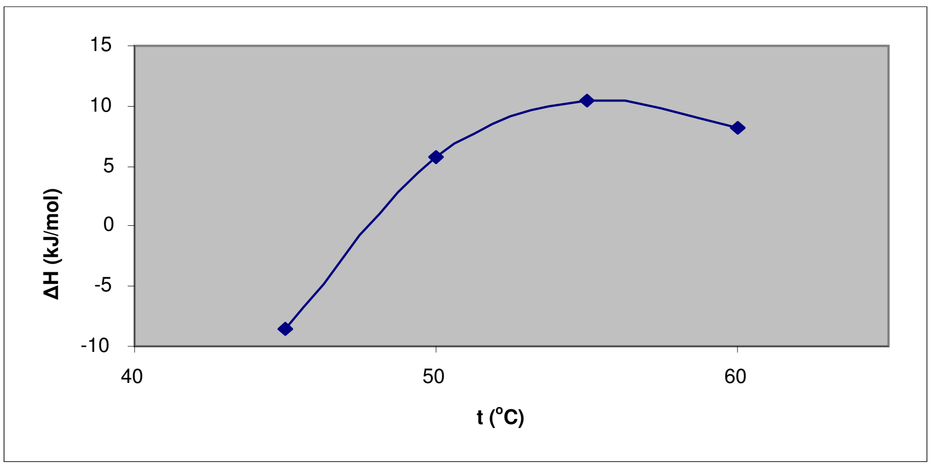

Figure B.70 : $\Delta H = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) KCl

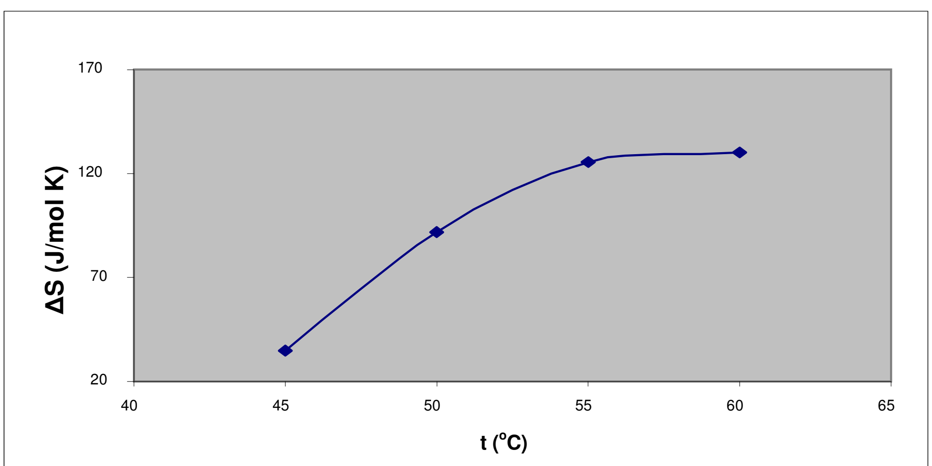

Figure B.71 : $\Delta S = f$ (t˚C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) KCl

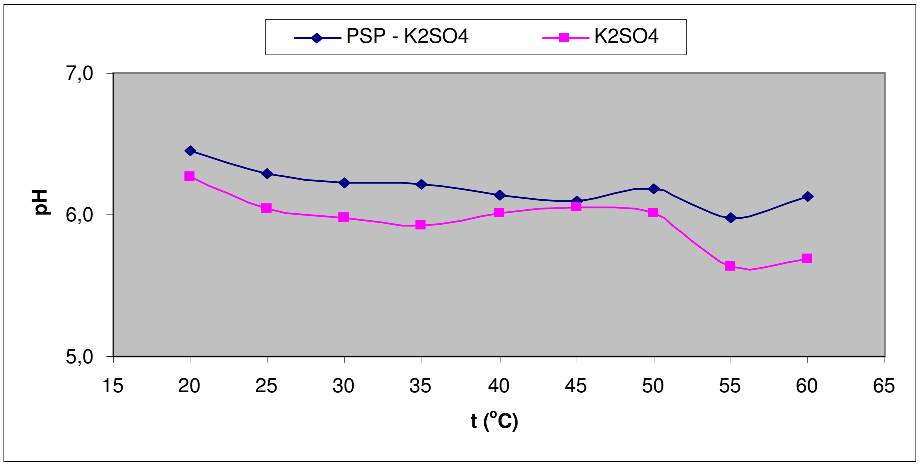

Figure B.72 : pH=*f* (t°C) curve of of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) K_2SO_4

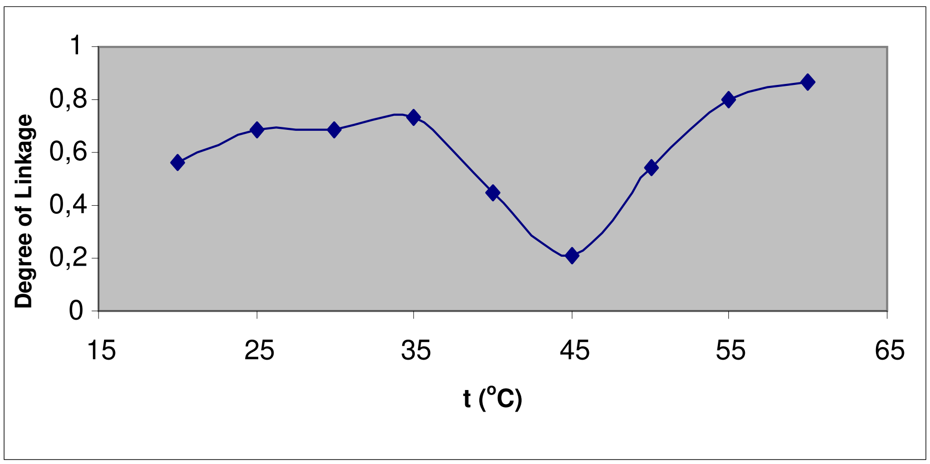

Figure B.73 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-1}$(mo/L) PSP – $1x10^{-1}$(mo/L) K_2SO_4

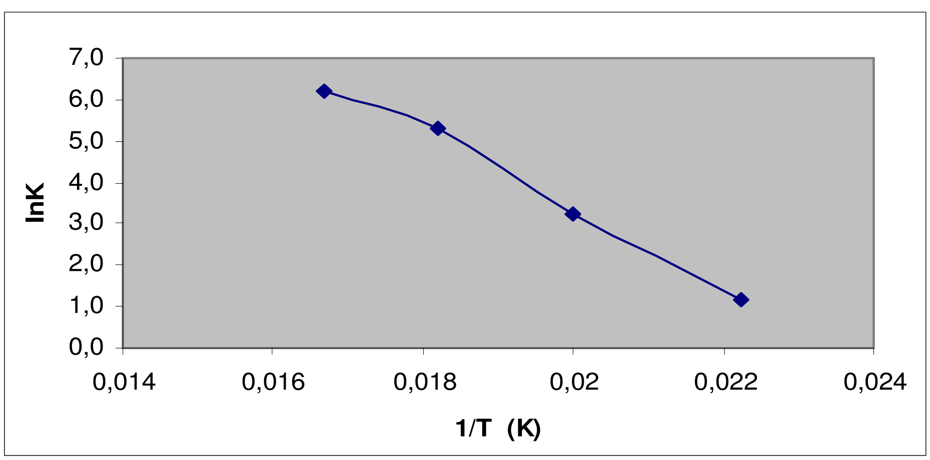

Figure B.74 : Curve of equilibrium constant $1x10^{-1}$(mo/L) PSP – $1x10^{-1}$(mo/L) K_2SO_4

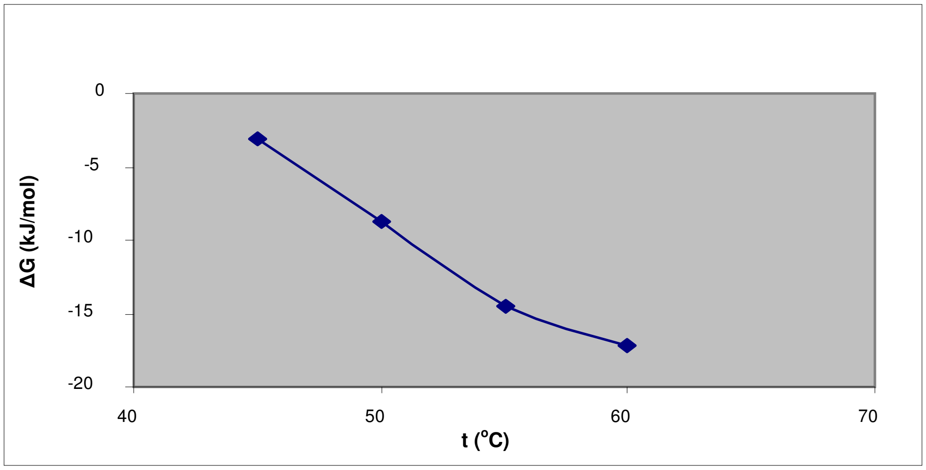

Figure B.75 : $\Delta G=f$ (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) K_2SO_4

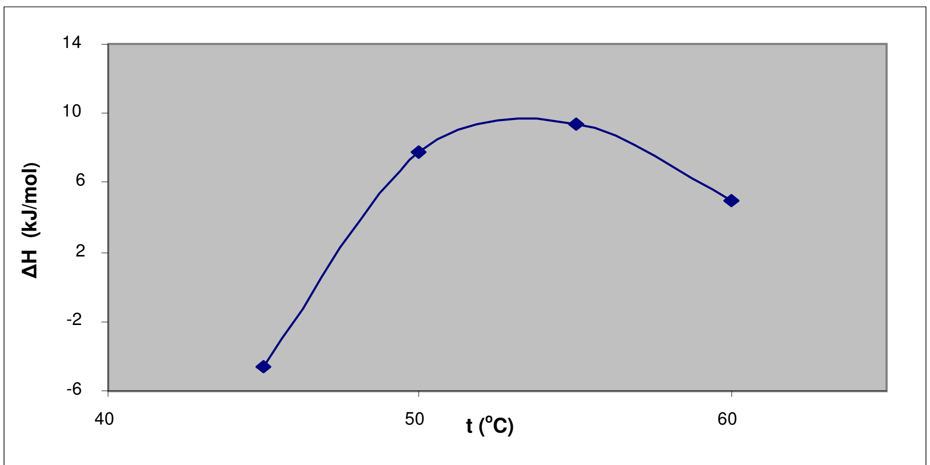

Figure B.76 : $\Delta H=f$ (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) K_2SO_4

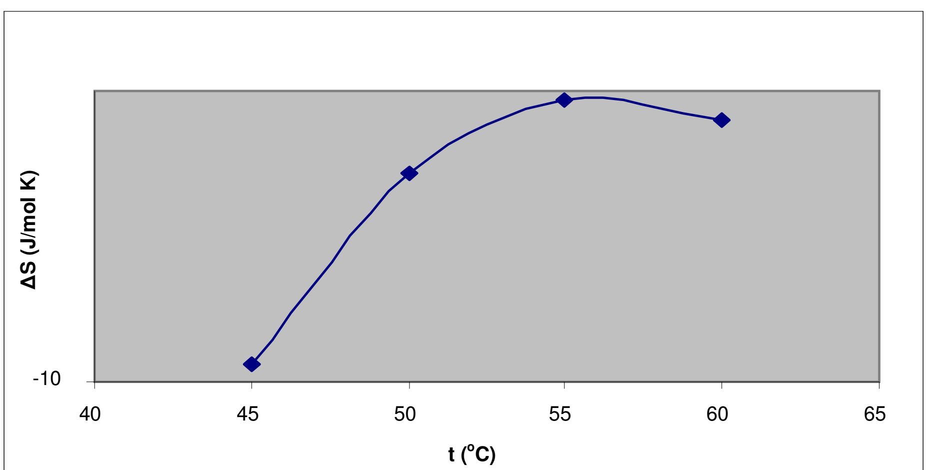

Figure B.77 : $\Delta S=f$ (t˚C) Curve of $1x10^{-1}$(mo/L) PSP - $1x10^{-1}$(mo/L) K_2SO_4

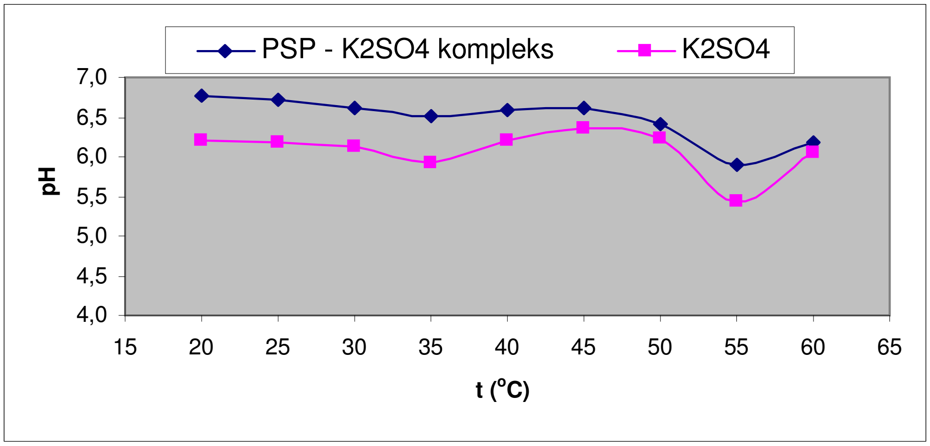

Figure B.78 : pH=f (t°C) curve of of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) K_2SO_4

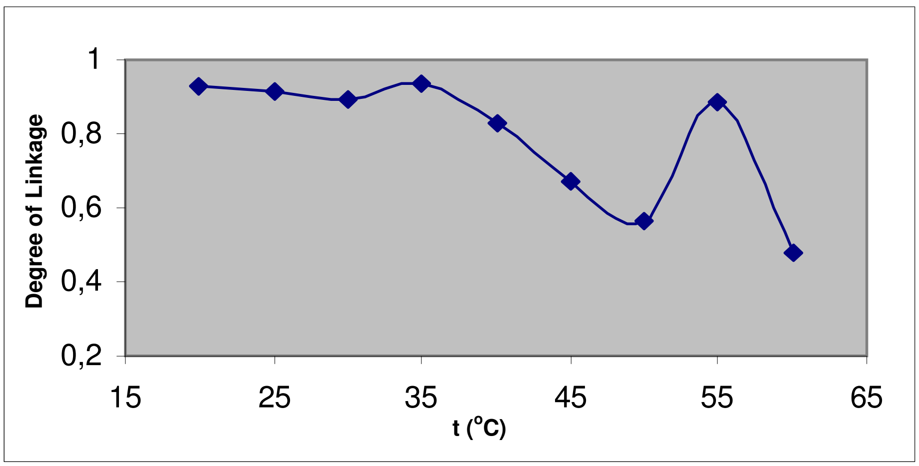

Figure B.79 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-2}$(mo/L) PSP – $1x10^{-2}$(mo/L) K_2SO_4

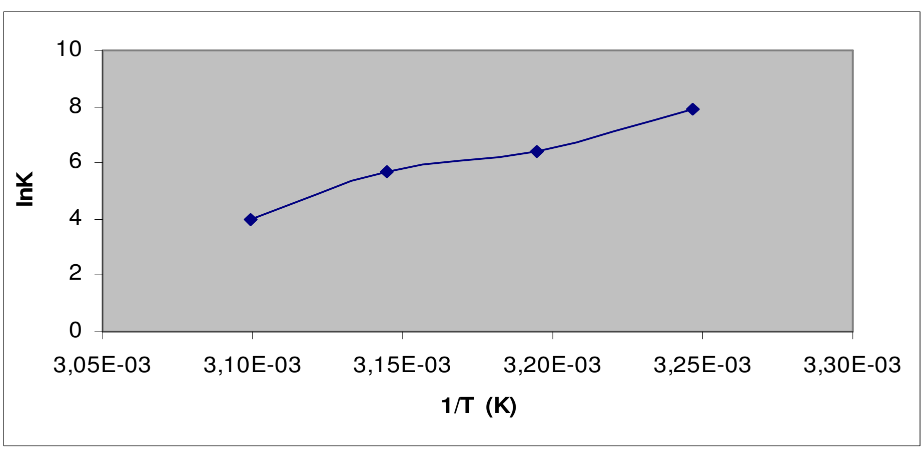

Figure B.80 : Curve of equilibrium constant $1x10^{-2}$(mo/L) PSP – $1x10^{-2}$(mo/L) K_2SO_4

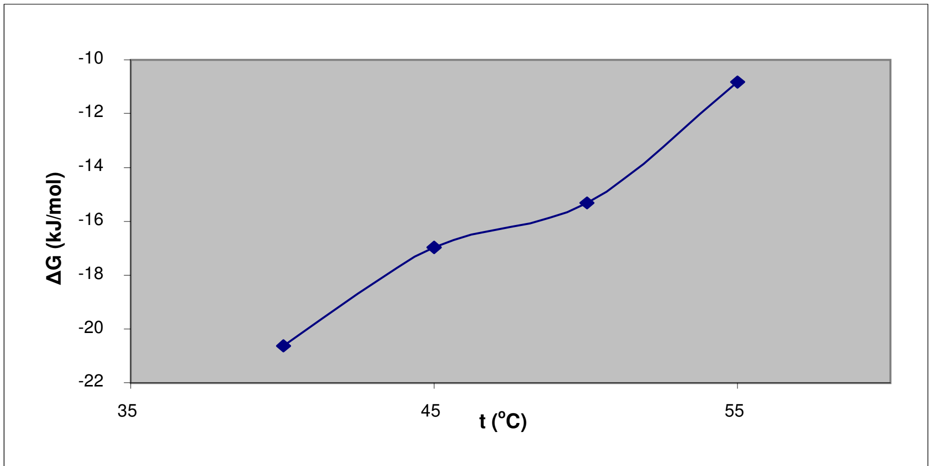

Figure B.81 : $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) K_2SO_4

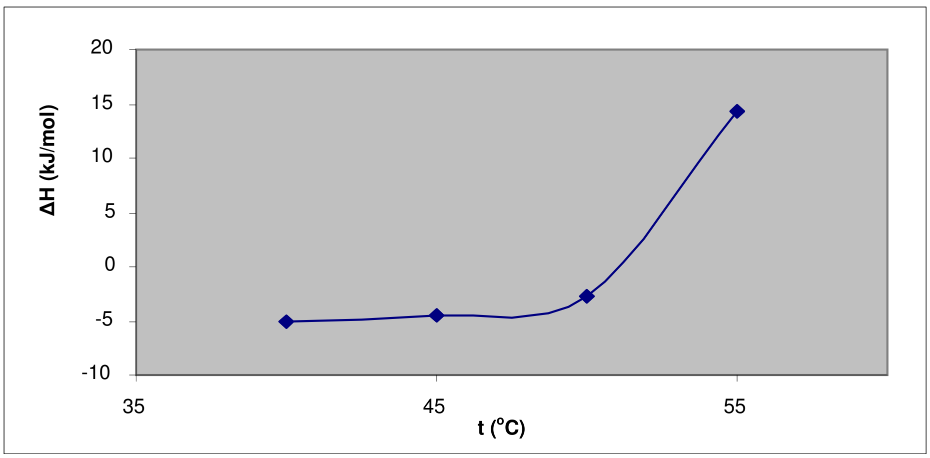

Figure B.82 : $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) K_2SO_4

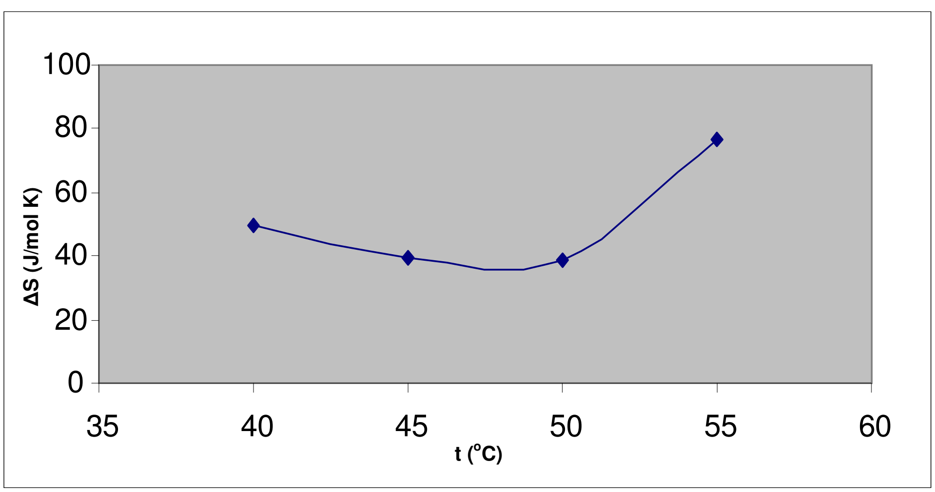

Figure B.83 : $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mo/L) PSP - $1x10^{-2}$(mo/L) K_2SO_4

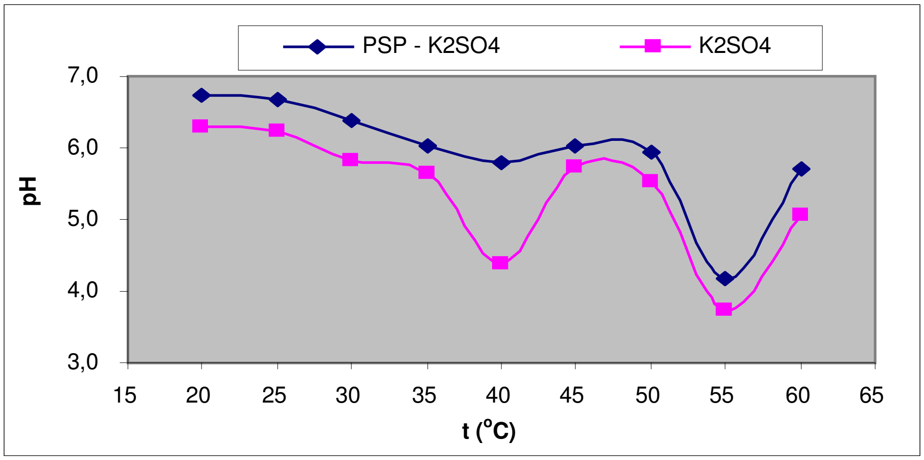

Figure B.84 : pH=f (t°C) curve of of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) K_2SO_4

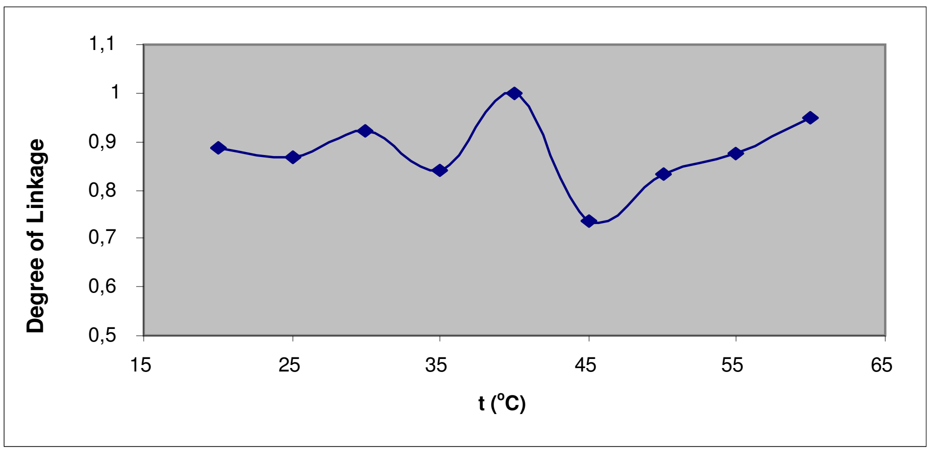

Figure B.85 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-3}$(mo/L) PSP – $1x10^{-3}$(mo/L) K_2SO_4

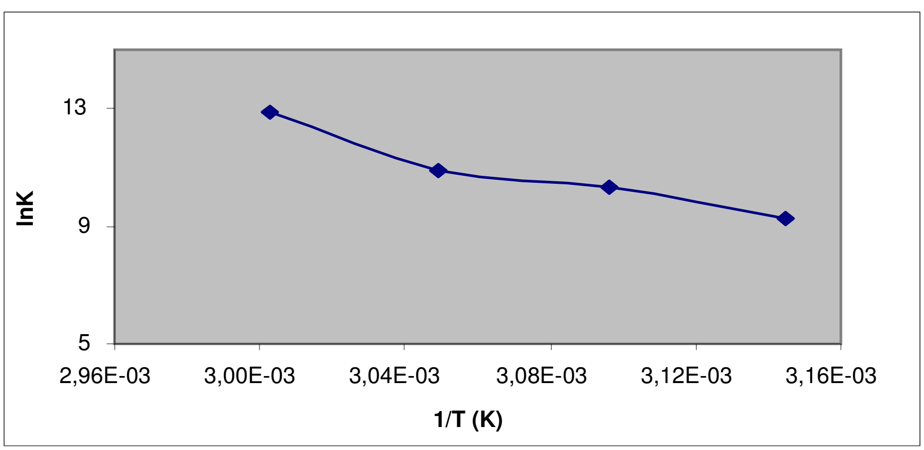

Figure B.86 : Curve of equilibrium constant $1x10^{-3}$(mo/L) PSP – $1x10^{-3}$(mo/L) K_2SO_4

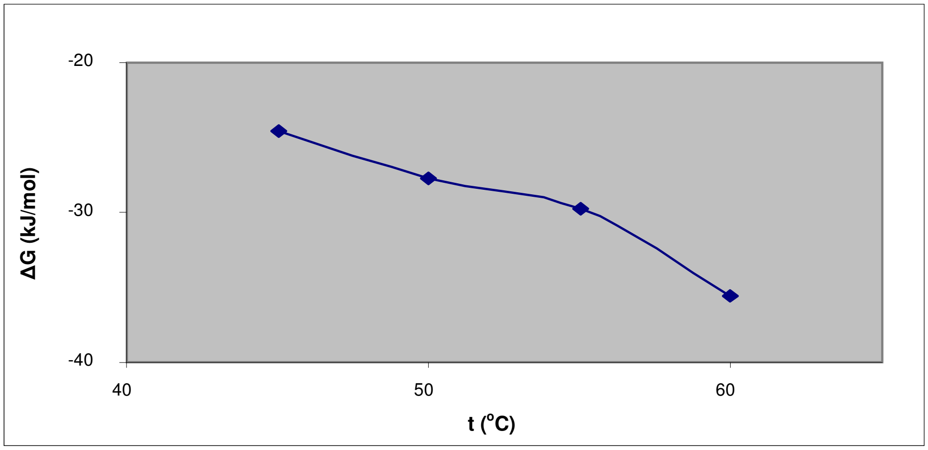

Figure B.87 : $\Delta G = f$ (t°C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) K_2SO_4

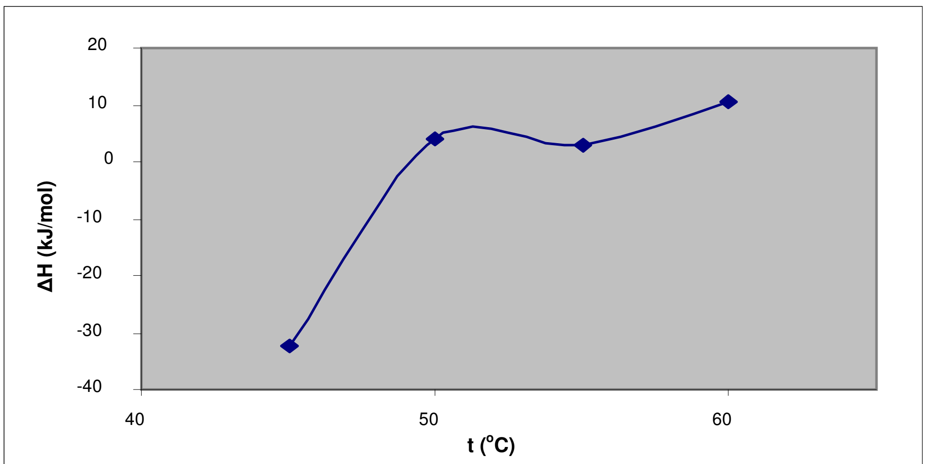

Figure B.88 : $\Delta H = f$ (t°C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) K_2SO_4

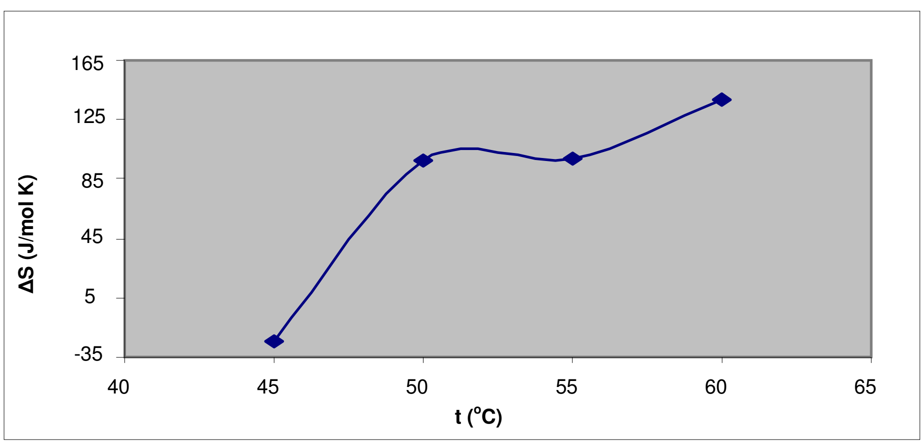

Figure B.89 : $\Delta S = f$ (t°C) Curve of $1x10^{-3}$(mo/L) PSP - $1x10^{-3}$(mo/L) K_2SO_4

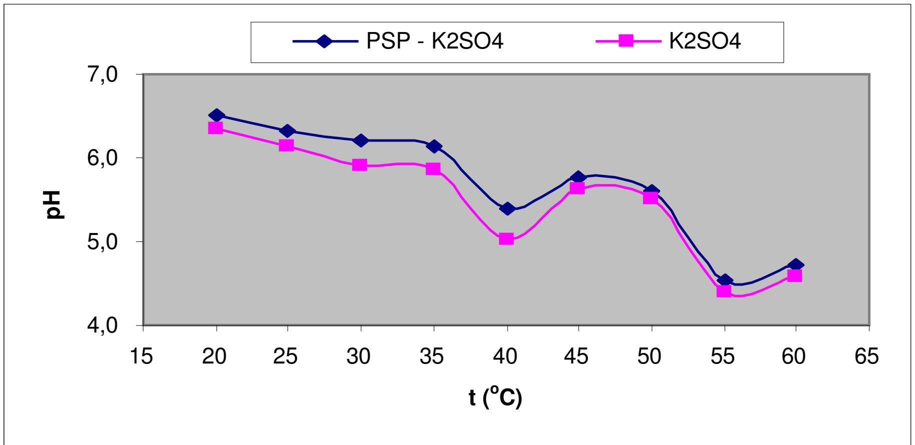

Figure B.90 : pH=f (t°C) curve of of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) K_2SO_4

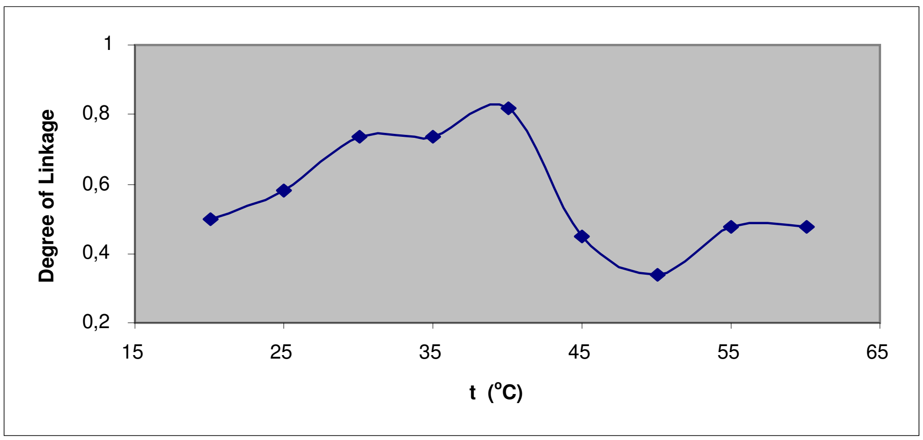

Figure B.91 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-4}$(mo/L) PSP – $1x10^{-4}$(mo/L) K_2SO_4

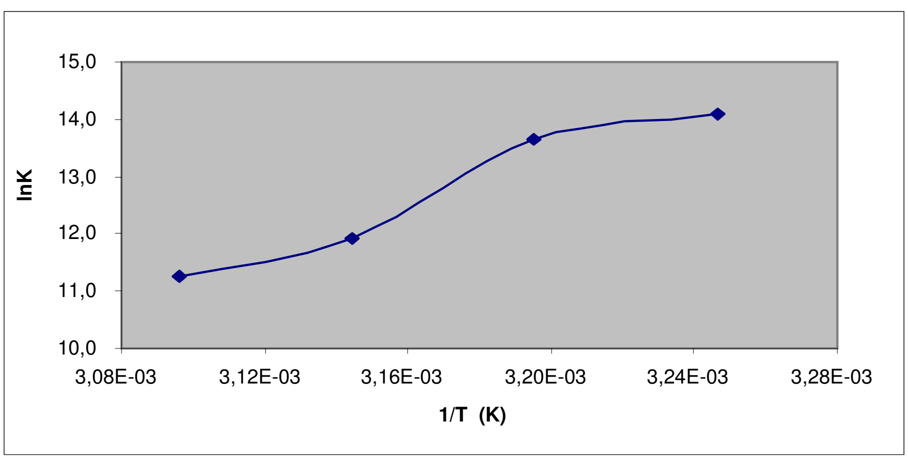

Figure B.92 : Curve of equilibrium constant $1x10^{-4}$(mo/L) PSP – $1x10^{-4}$(mo/L) K_2SO_4

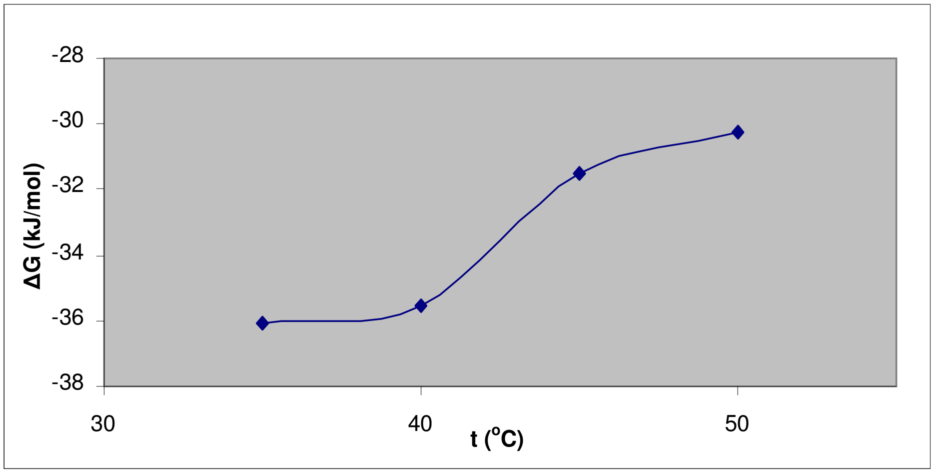

Figure B.93 : $\Delta G = f$ (t°C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) K_2SO_4

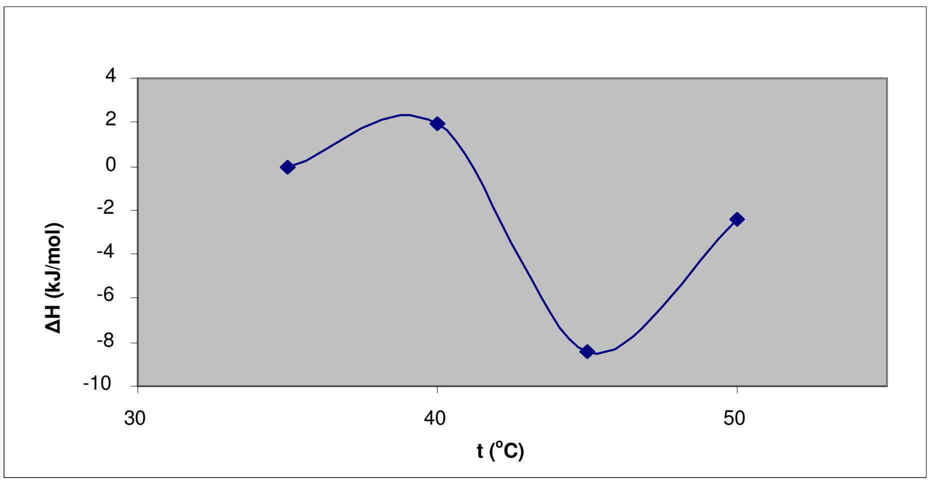

Figure B.94 : $\Delta H = f$ (t°C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) K_2SO_4

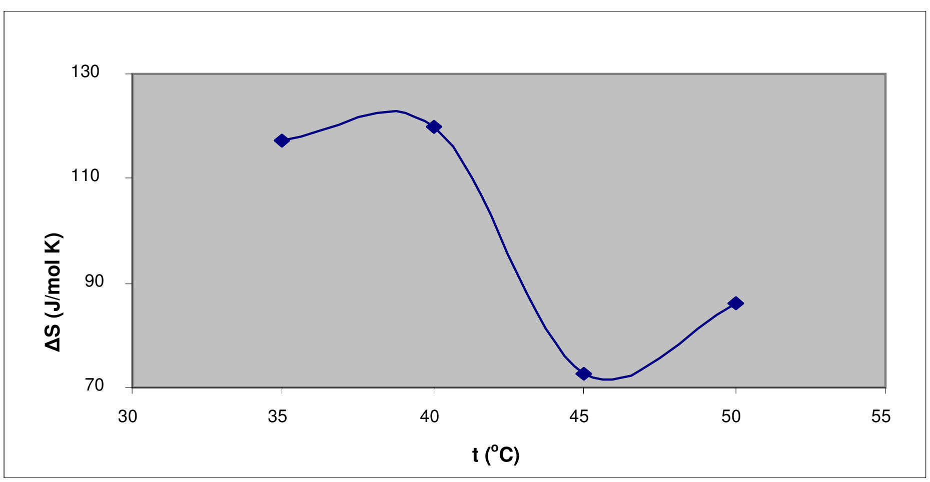

Figure B.95 : $\Delta S = f$ (t°C) Curve of $1x10^{-4}$(mo/L) PSP - $1x10^{-4}$(mo/L) K_2SO_4

APPENDİX C: Figures of Thermodynamic Results for PSP-Salt (I=Constant)

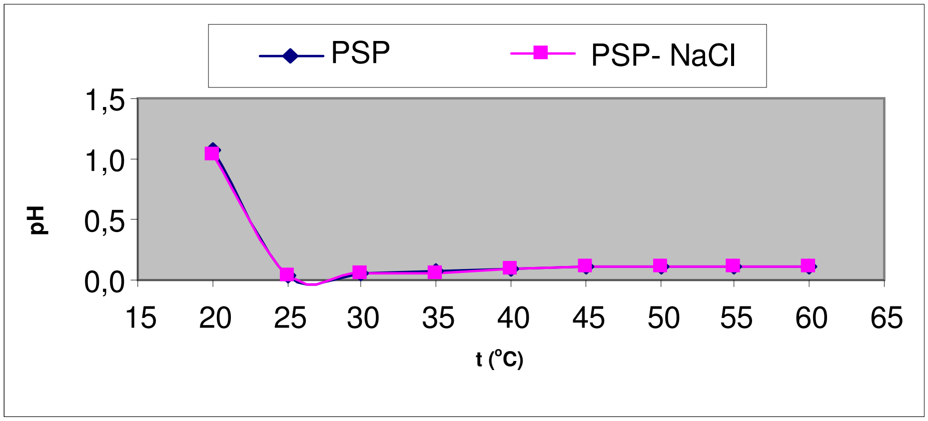

Figure C. 1: pH=f (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

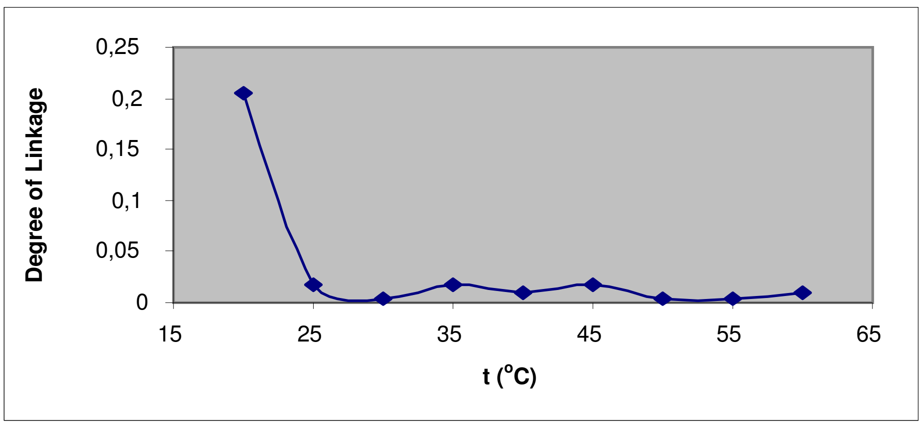

Figure C.1: Degree of linkage, θ =f (t°C) Curve $1x10^{-1}$(mol/L) PSP – $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

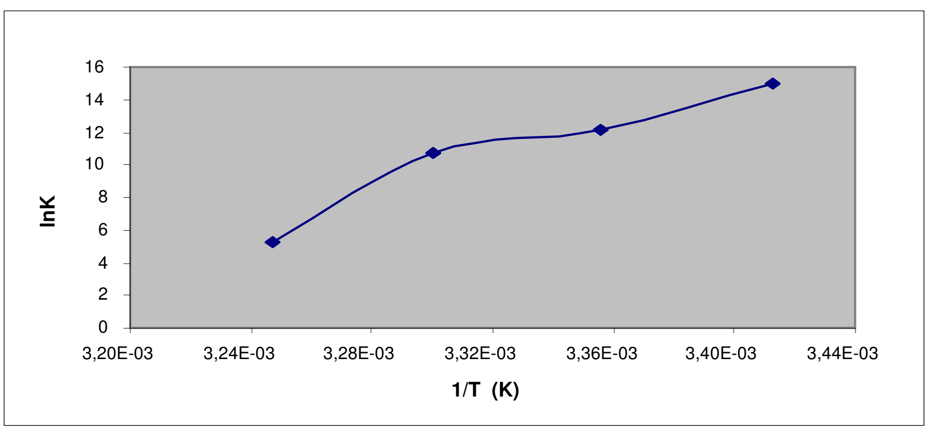

Figure C. 2: Curve of equilibrium constant $1x10^{-1}$(mol/L) PSP – $1x10^{-1}$(mol/L),NaCl, (I=1 mol/L)

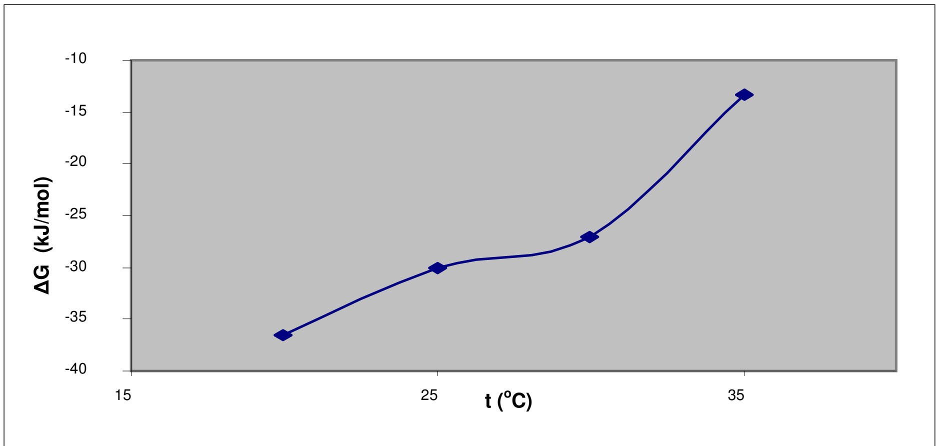

Figure C. 3: $\Delta G = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

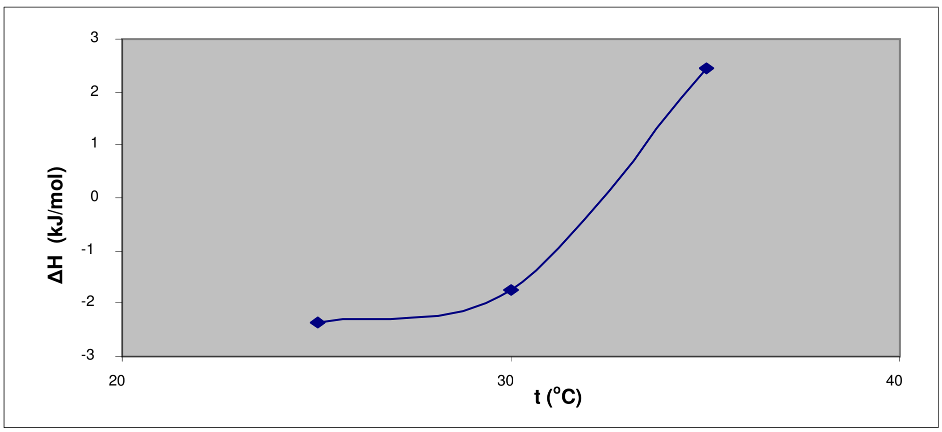

Figure C. 4: $\Delta H = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

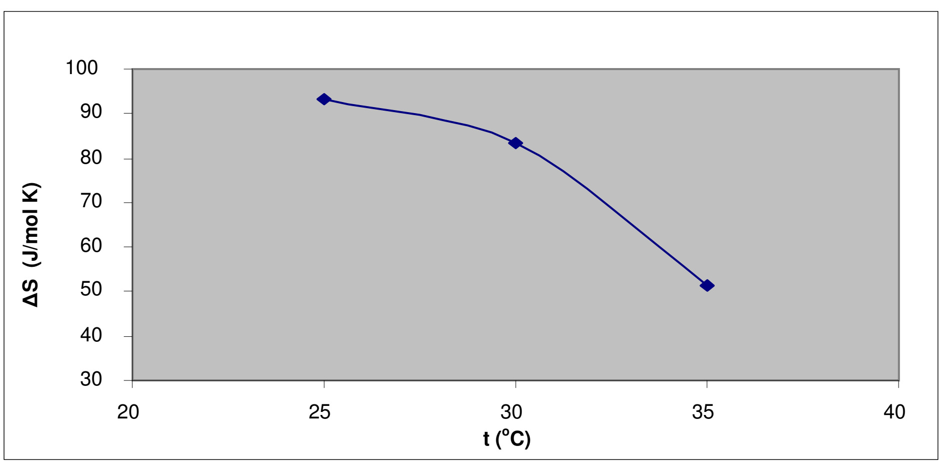

Figure C. 5: $\Delta S = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

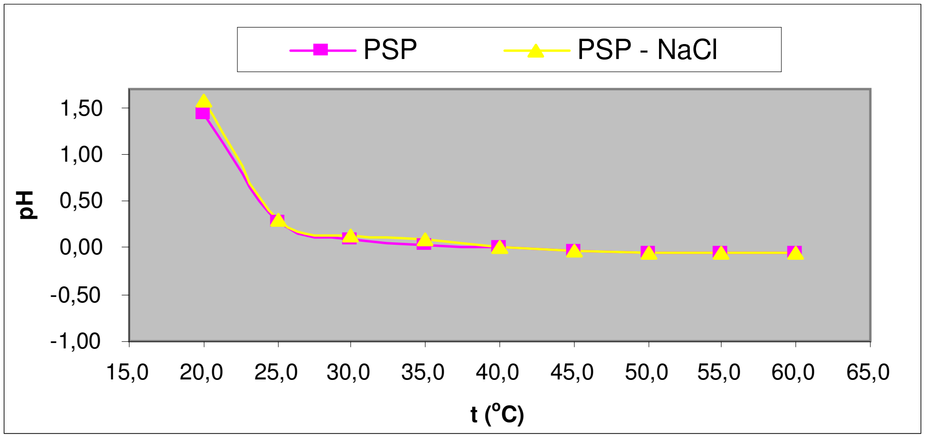

Figure C. 6: pH=*f* (t˚C) Curve 1x10^{-2}(mol/L) PSP - 1x10^{-2}(mol/L) NaCl, (I=1x10^{-1} mol/L)

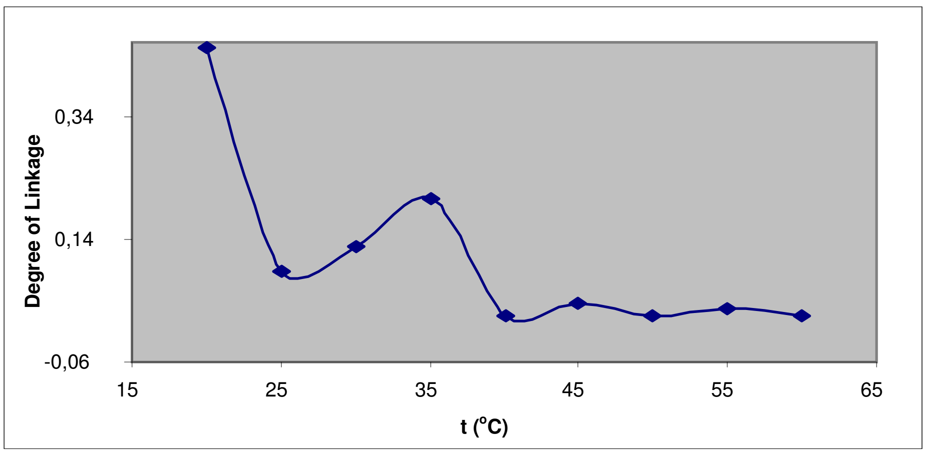

Figure C.7 :Degree of linkage, θ =*f* (t˚C) Curve 1x10^{-2}(mol/L) PSP – 1x10^{-2}(mol/L) NaCl, (I=1x10^{-1} mol/L)

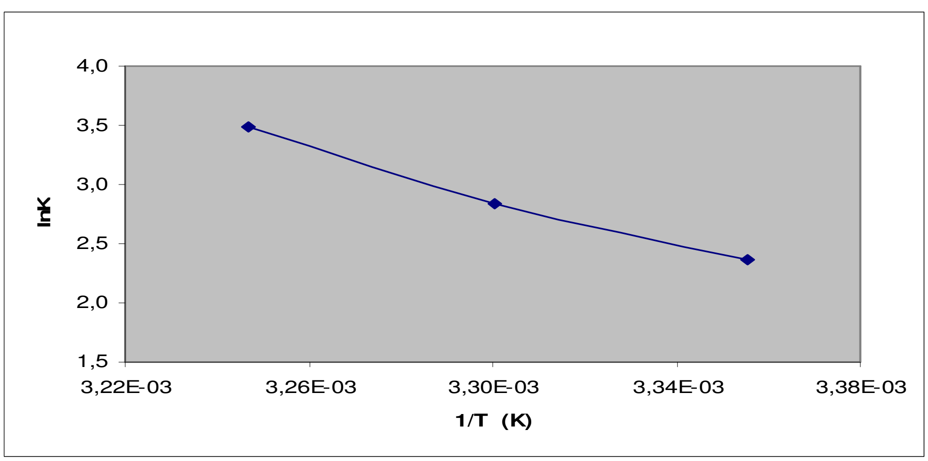

Figure C. 8: Curve of equilibrium constant 1x10^{-2}(mol/L) PSP - 1x10^{-2}(mol/L) NaCl, (I=1x10^{-1} mol/L)

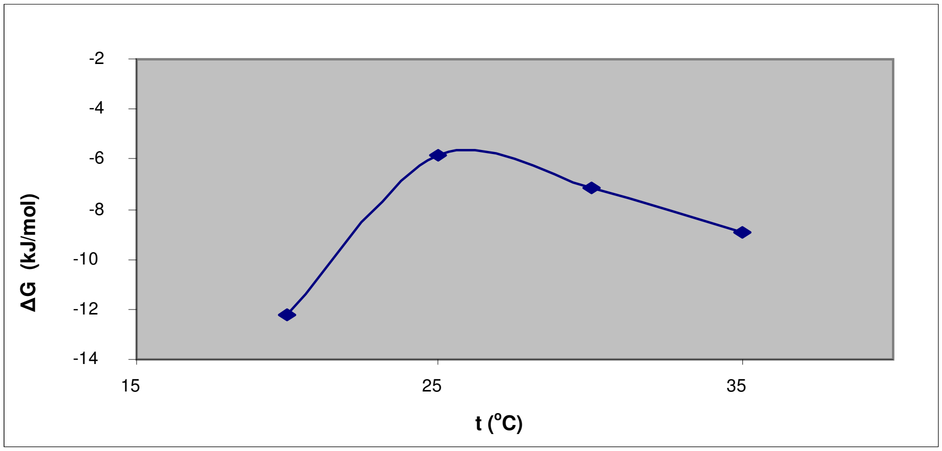

Figure C. 9: $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) NaCl, (I=$1x10^{-1}$ mol/L)

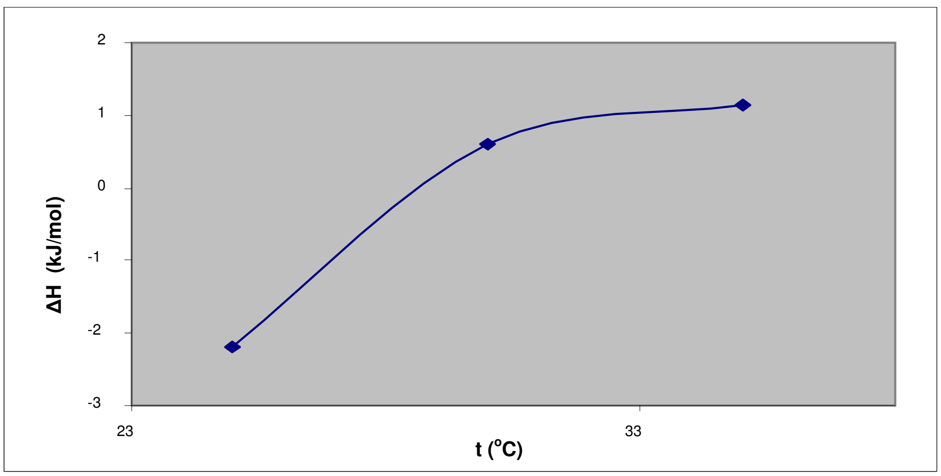

Figure C. 10: $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) NaCl, (I=$1x10^{-1}$ mol/L)

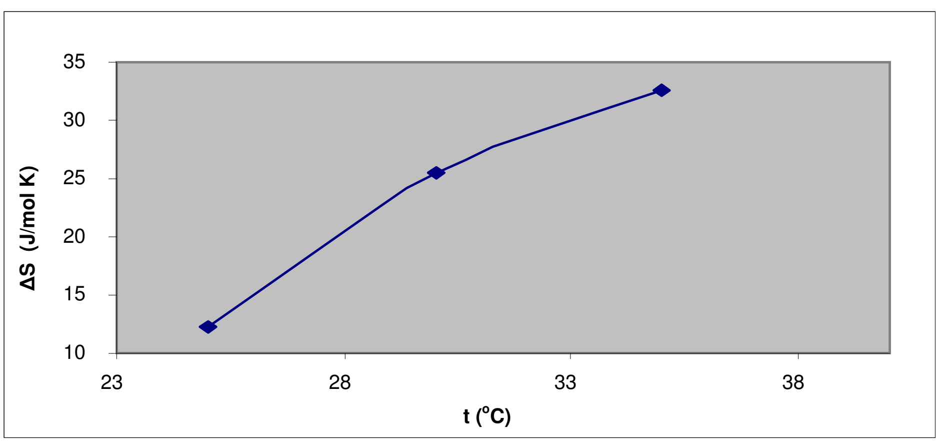

Figure C. 11: $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) NaCl, (I=$1x10^{-1}$ mol/L)

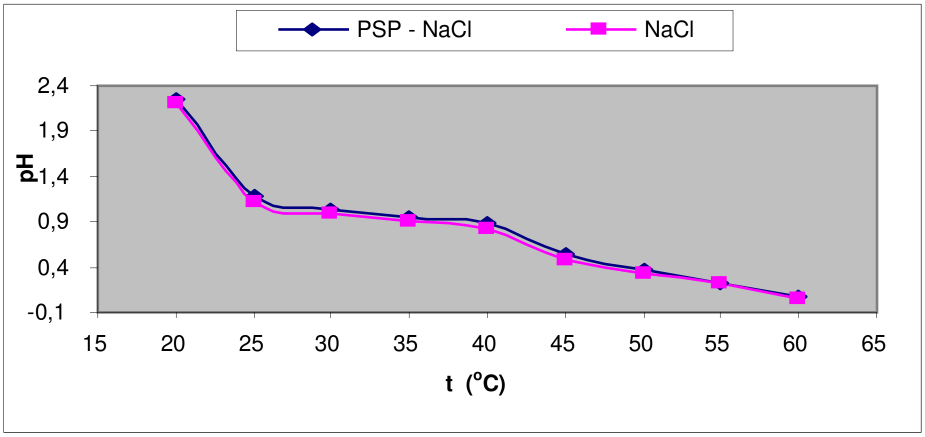

Figure C. 12: pH=*f* (t°C) Curve 1x10^{-3}(mol/L) PSP - 1x10^{-3}(mol/L) NaCl, (I=1x10^{-2} mol/L)

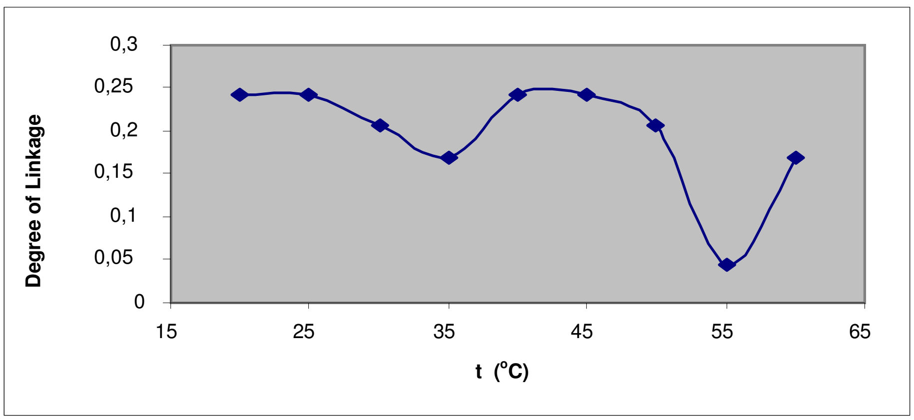

Figure C. 13: Degree of linkage, θ =*f* (t°C) Curve 1x10^{-3}(mol/L) PSP – 1x10^{-3}(mol/L) NaCl, (I=1x10^{-2} mol/L)

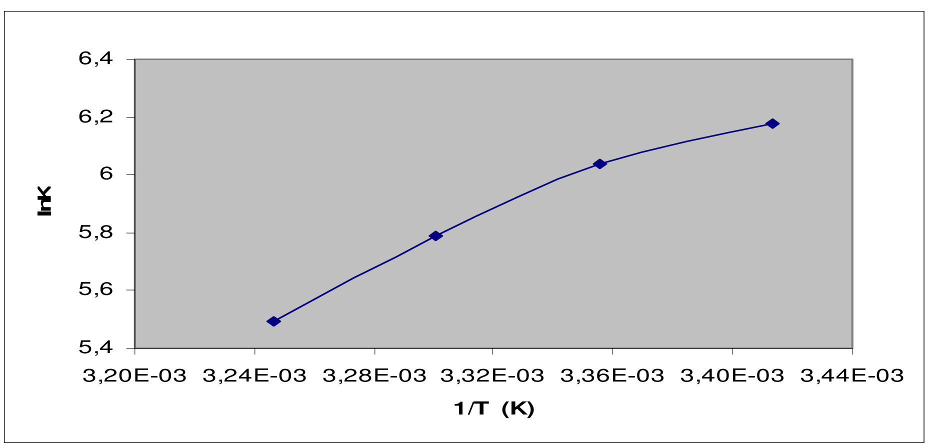

Figure C. 14: Curve of equilibrium constant 1x10^{-3}(mol/L) PSP - 1x10^{-3}(mol/L) NaCl, (I=1x10^{-2} mol/L)

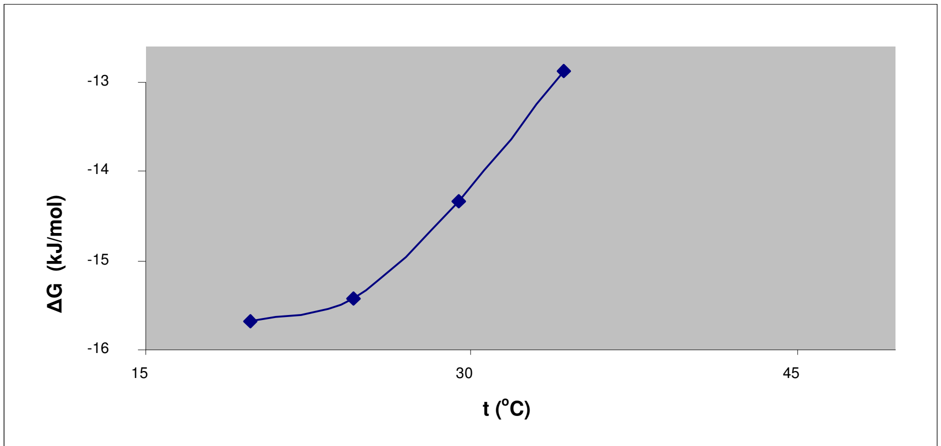

Figure C. 15: $\Delta G = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP - $1x10^{-3}$(mol/L) NaCl, (I=$1x10^{-2}$ mol/L)

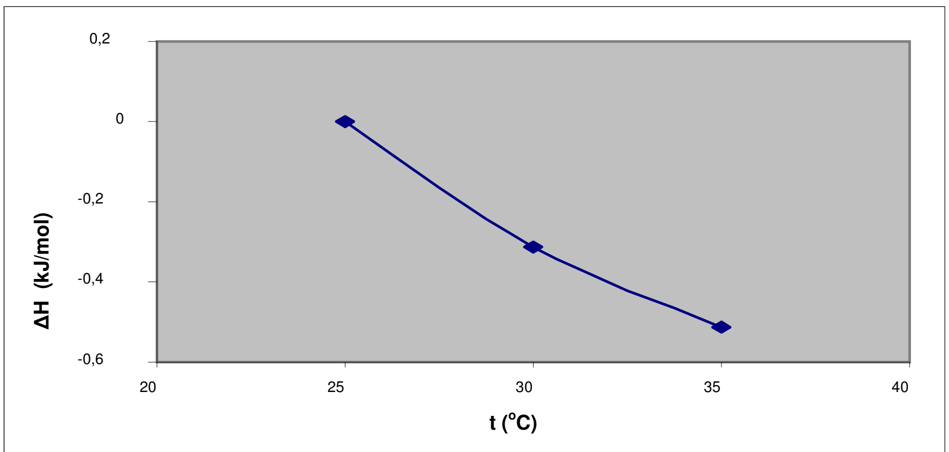

Figure C. 16: $\Delta H = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP - $1x10^{-3}$(mol/L) NaCl, (I=$1x10^{-2}$ mol/L)

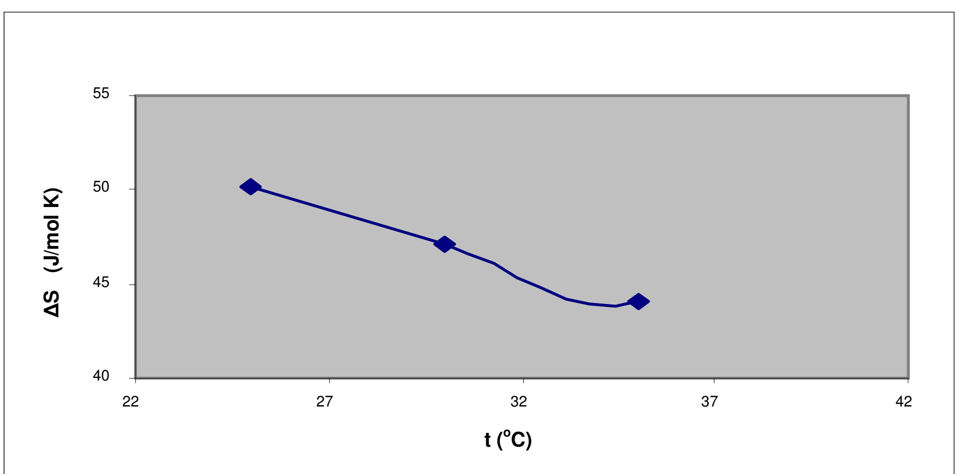

Figure C. 17: $\Delta S = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP - $1x10^{-3}$(mol/L) NaCl, (I=$1x10^{-2}$ mol/L)

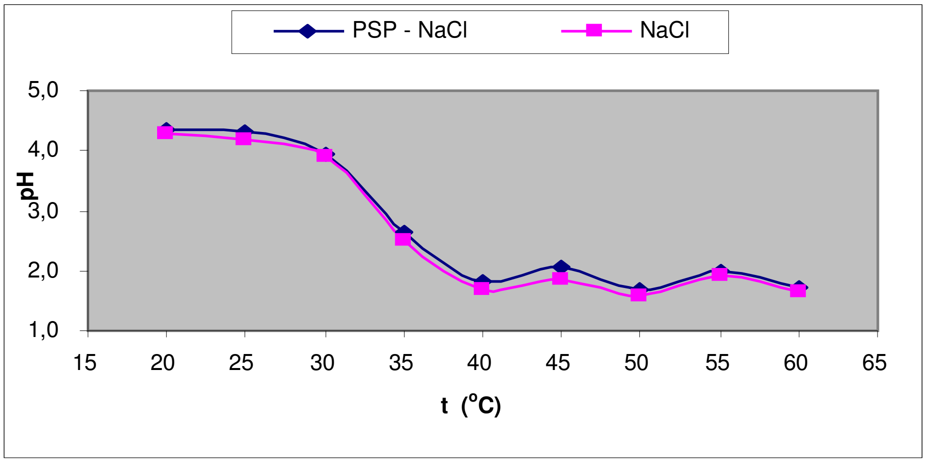

Figure C. 18: pH=f (t°C) Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) NaCl, (I=$1x10^{-3}$ mol/L)

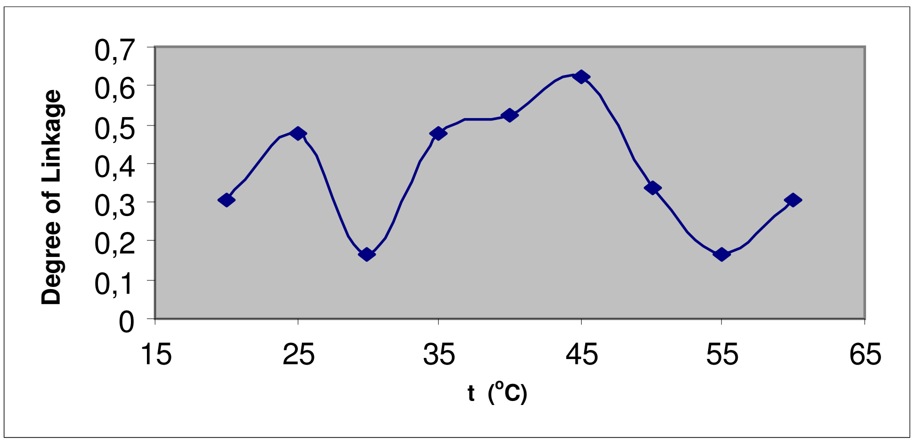

Figure C. 19: Degree of linkage, θ =f (t°C) Curve $1x10^{-4}$(mol/L)PSP - $1x10^{-4}$(mol/L) NaCl, (I=$1x10^{-3}$ mol/L)

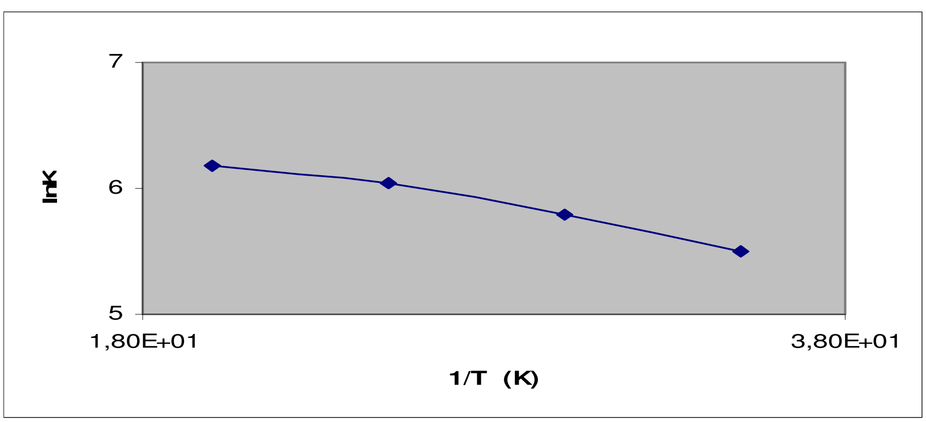

Figure C. 20: Curve of equilibrium constant $1x10^{-4}$(mol/L) PSP -$1x10^{-4}$(mol/L) NaCl (I=$1x10^{-3}$ mol/L)

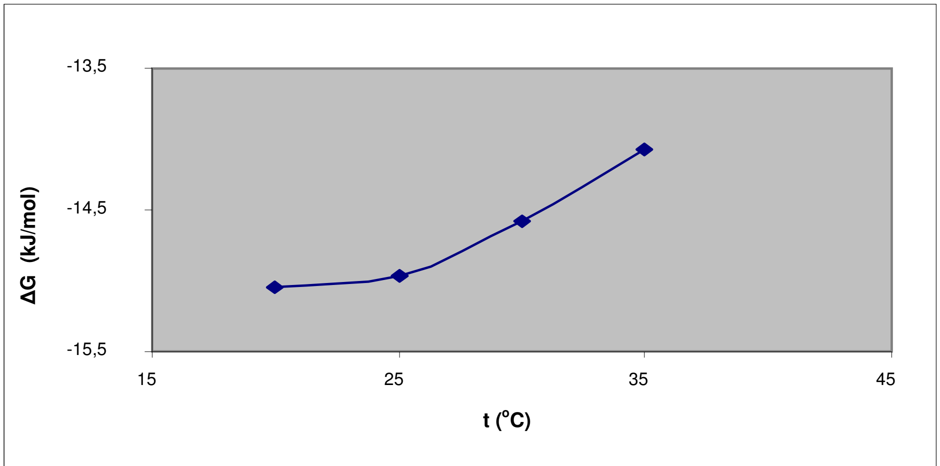

Figure C. 21: $\Delta G=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) NaCl, ($I=1x10^{-3}$ mol/L)

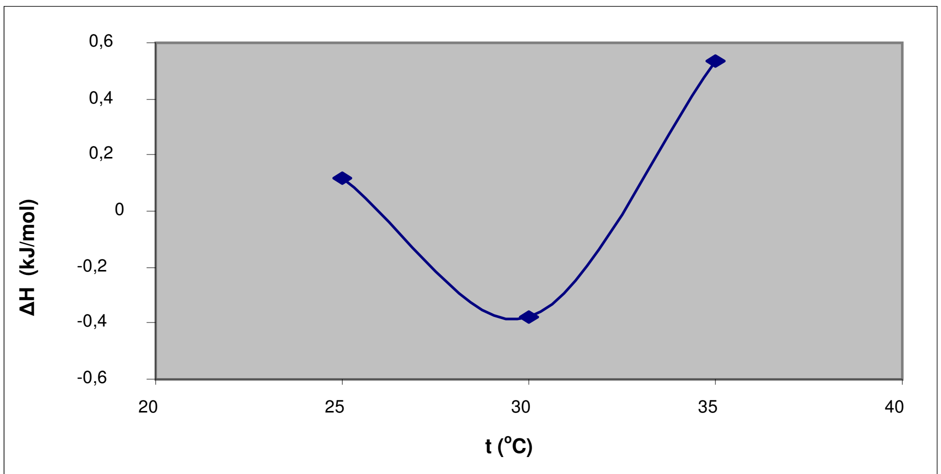

Figure C. 22: $\Delta H=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) NaCl, ($I=1x10^{-3}$ mol/L)

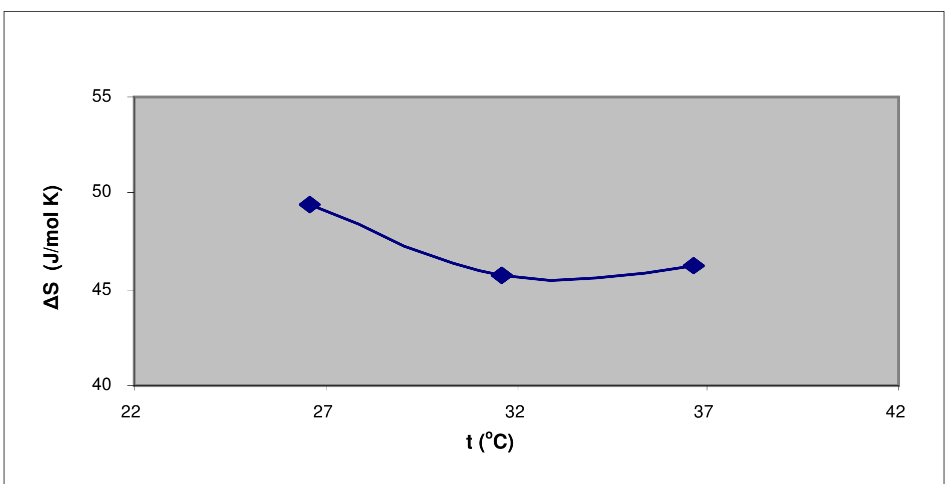

Figure C. 23: $\Delta S=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) NaCl, ($I=1x10^{-3}$ mol/L)

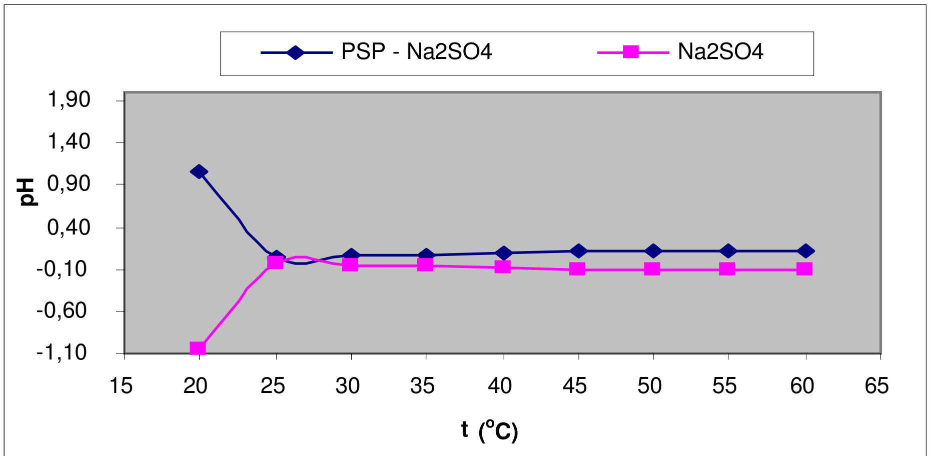

Figure C. 24: pH=f (t°C) Curve $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) Na_2SO_4, (I=1 mol/L)

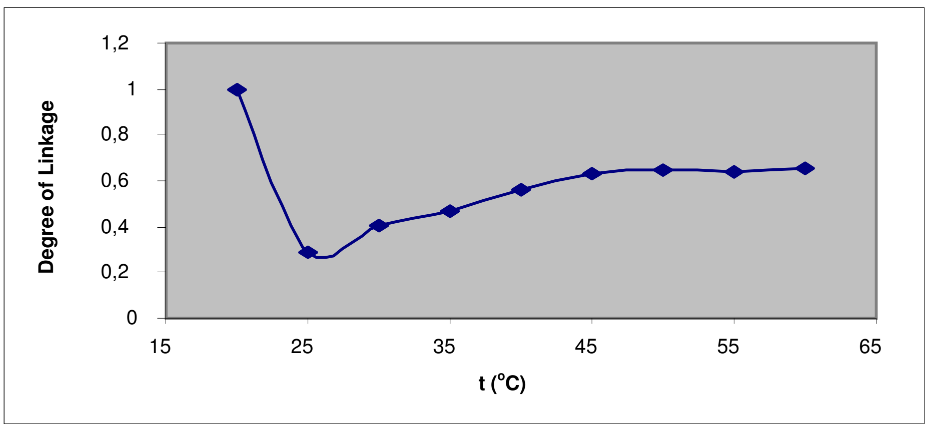

Figure C. 25: Degree of linkage, θ =f (t°C) curve $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) Na_2SO_4, (I=1 mol/L)

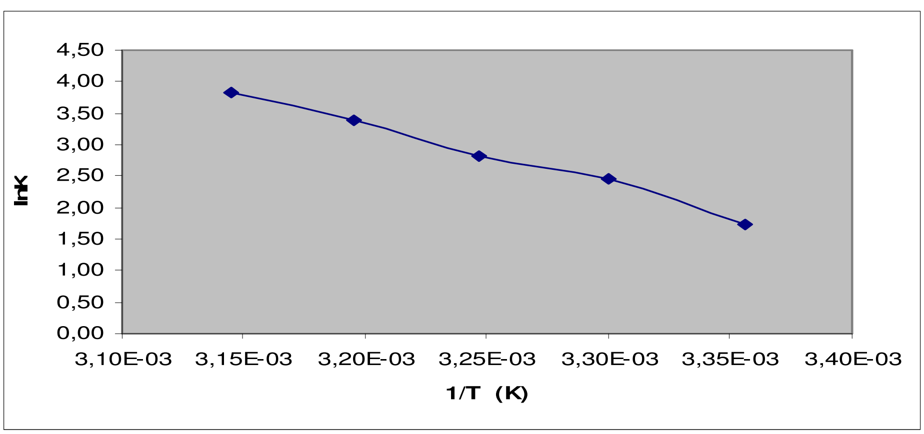

Figure C. 26: Curve of equilibrium constant $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L)Na_2SO_4, (I=1 mol/L)

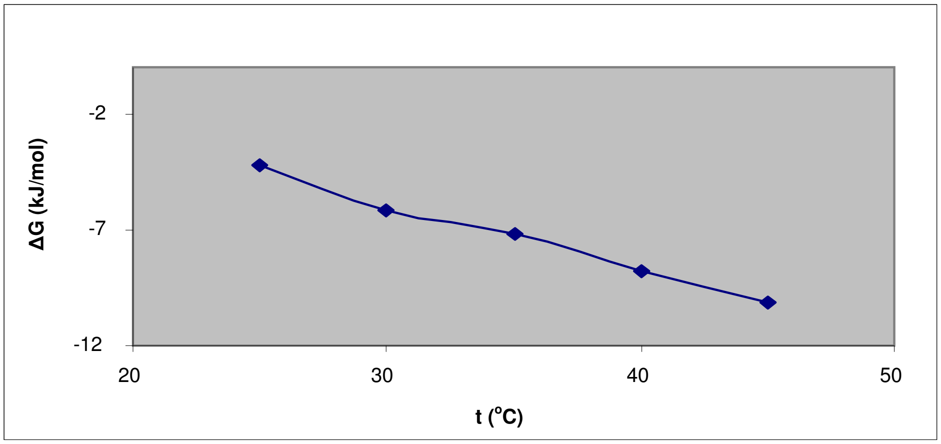

Figure C. 27: $\Delta G=f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) Na_2SO_4, (I=1 mol/L)

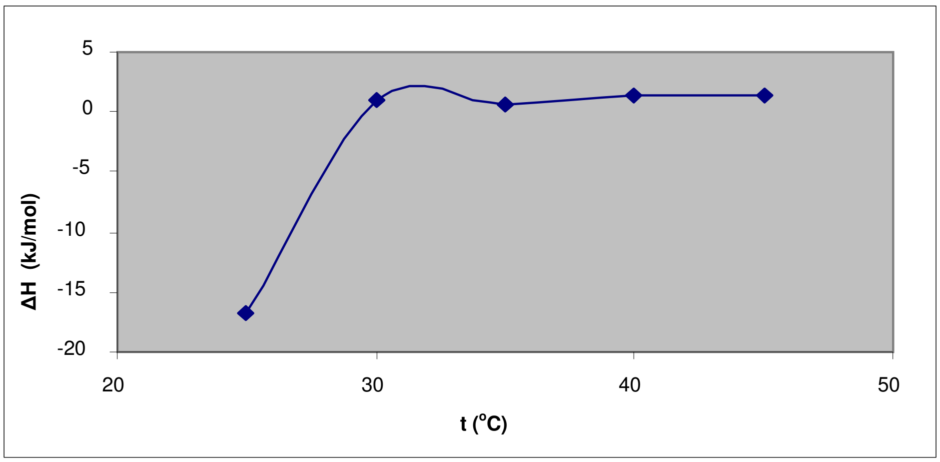

Figure C. 28: $\Delta H=f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) Na_2SO_4, (I=1 mol/L)

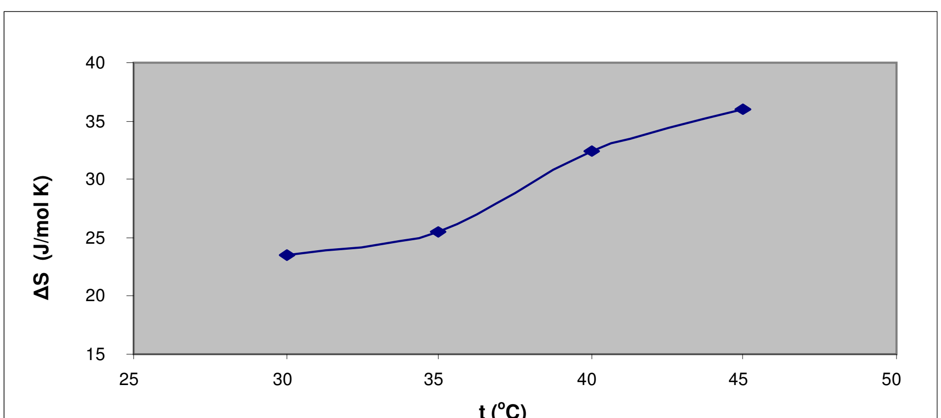

Figure C. 29: $\Delta S=f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP - $1x10^{-1}$(mol/L) Na_2SO_4, (I=1 mol/L)

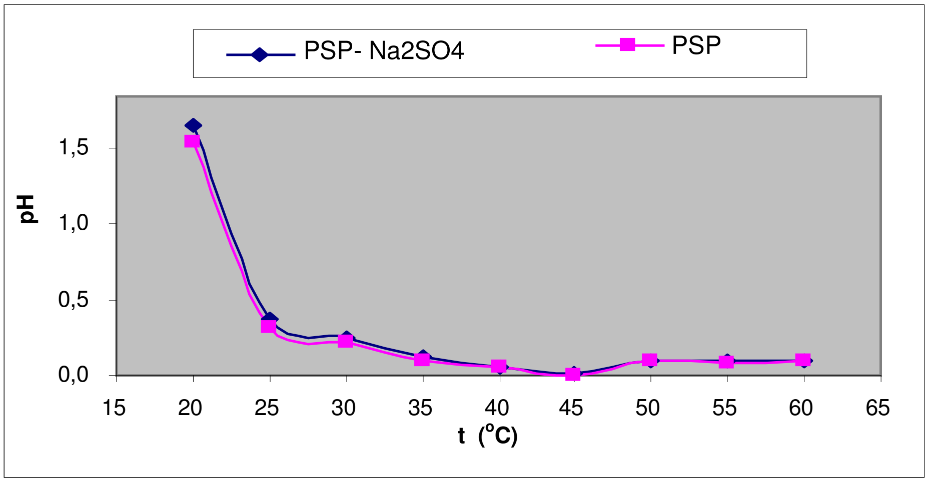

Figure C. 30: pH=*f* (t°C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) Na_2SO_4, (I=$1x10^{-1}$ mol/L)

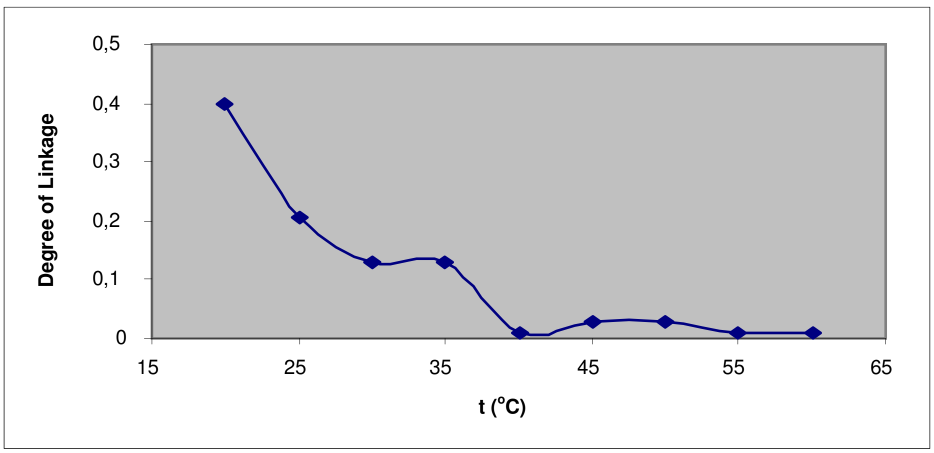

Figure C. 31: Degree of linkage, θ =*f* (t°C) Curve $1x10^{-2}$(mol/L) PSP – $1x10^{-2}$(mol/L) Na_2SO_4, (I=$1x10^{-1}$ mol/L)

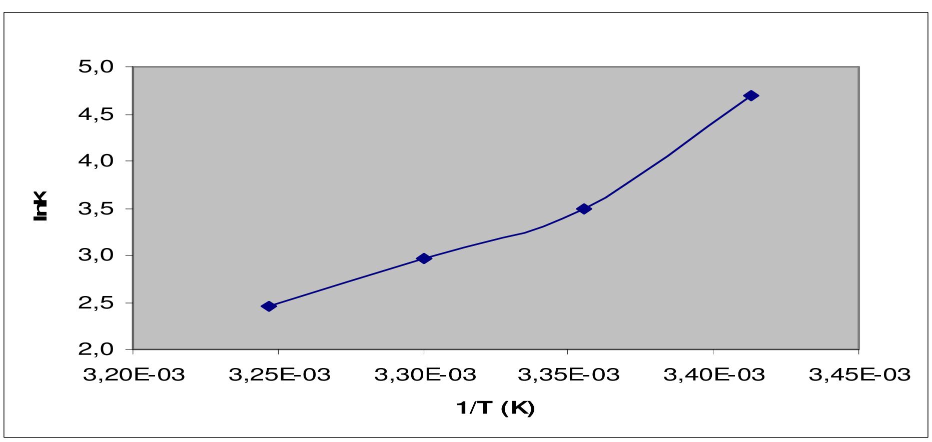

Figure C. 32: Curve of equilibrium constant $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) Na_2SO_4, (I=$1x10^{-1}$ mol/L)

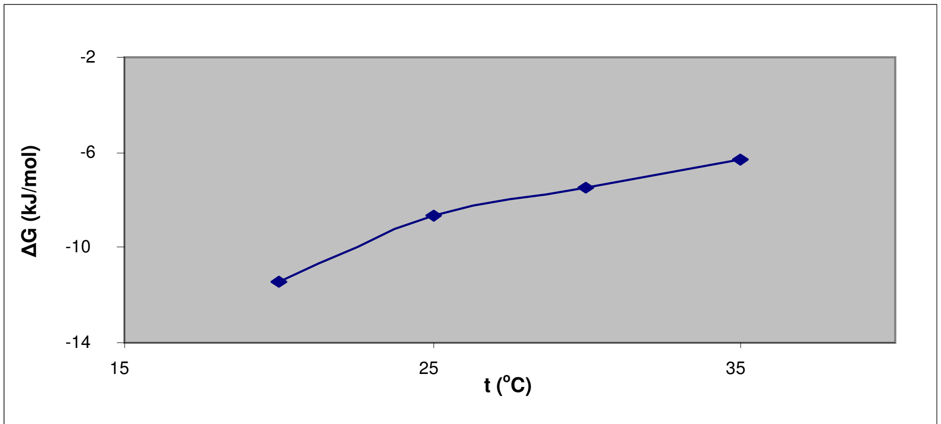

Figure C. 33: $\Delta G=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) Na_2SO_4, ($I=1x10^{-1}$ mol/L)

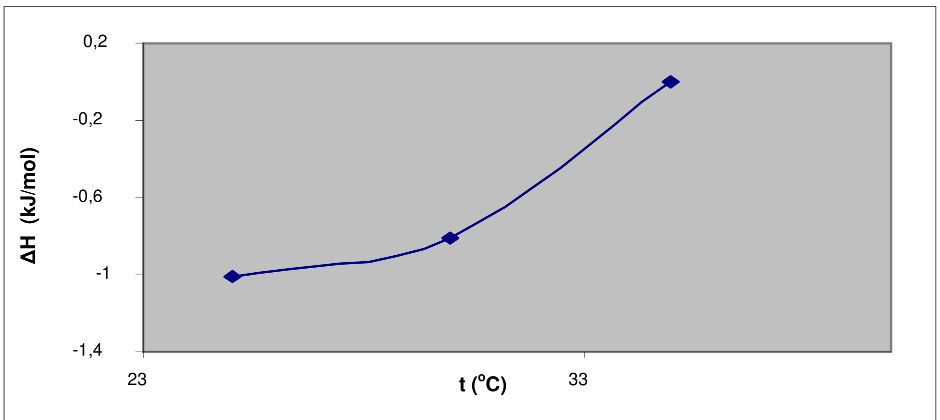

Figure C. 34: $\Delta H=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) Na_2SO_4, ($I=1x10^{-1}$ mol/L)

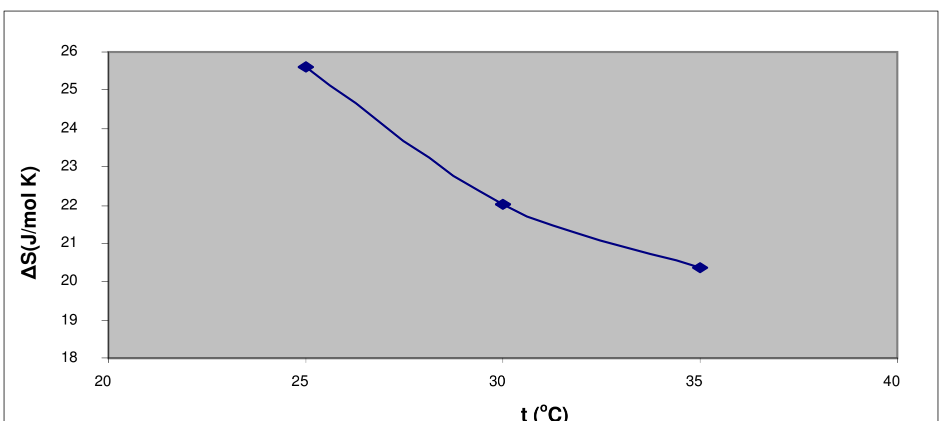

Figure C. 35: $\Delta S=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP - $1x10^{-2}$(mol/L) Na_2SO_4 , ($I=1x10^{-1}$ mol/L)

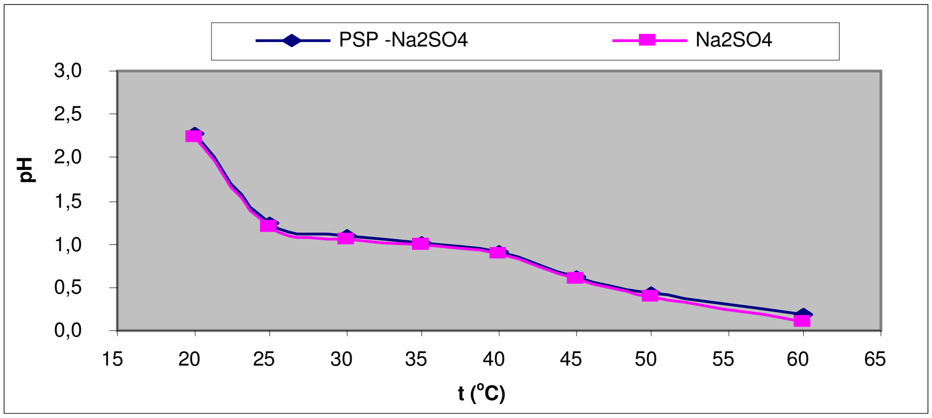

Figure C. 36: pH=f (t°C) Curve $1x10^{-3}$(mol/L) PSP - $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

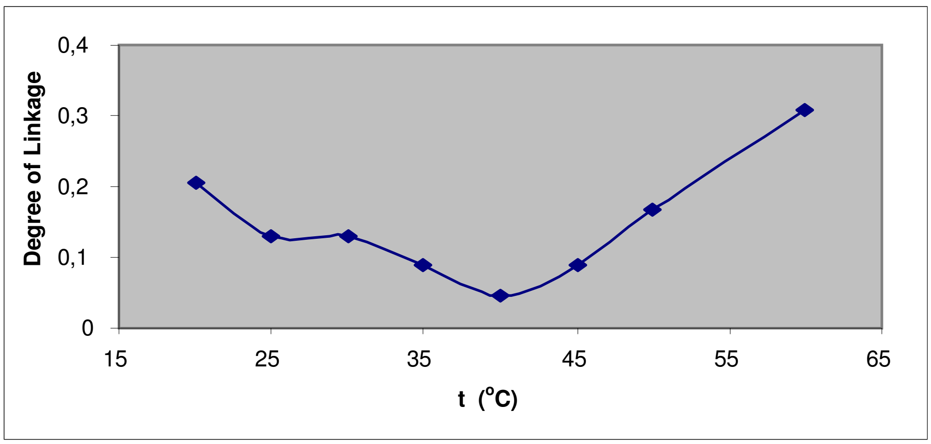

Figure C. 37: Degree of linkage, $\theta = f$ (t°C) Curve $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

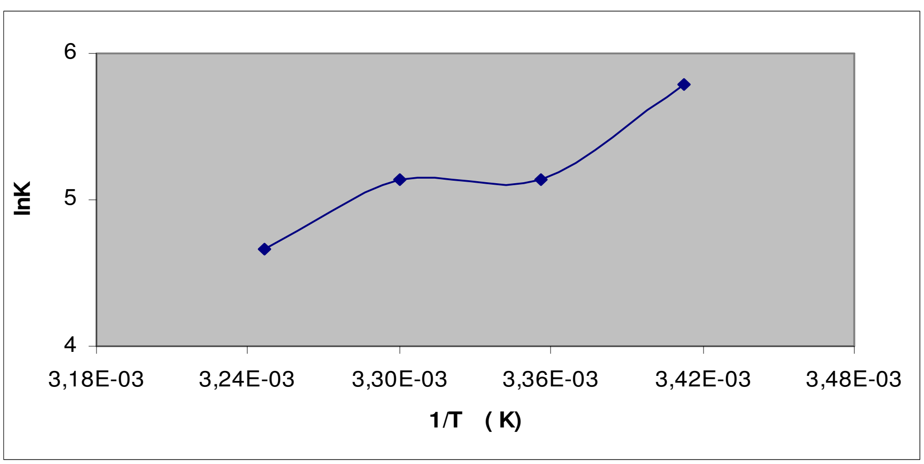

Figure C. 38: Curve of equilibrium constant $1x10^{-3}$(mol/L) PSP - $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

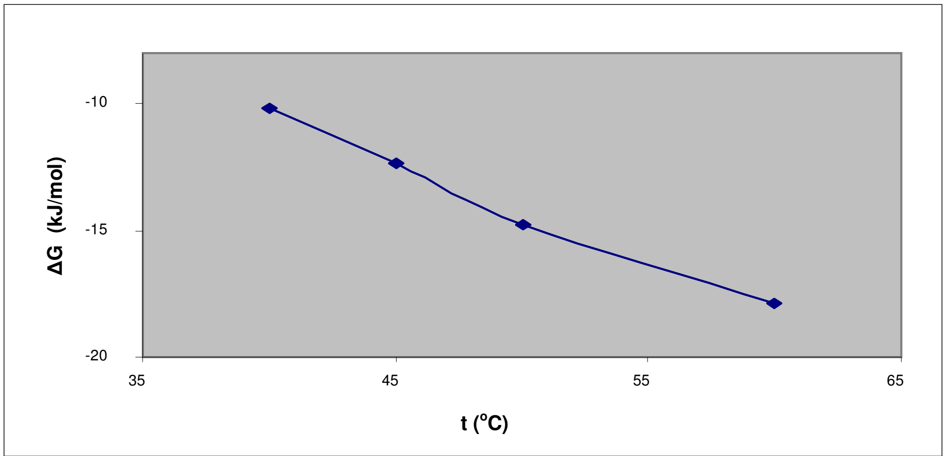

Figure C. 39: $\Delta G = f$ (t˚C) Curve of 1×10^{-3}(mol/L) PSP - 1×10^{-3}(mol/L) Na_2SO_4, ($I = 1 \times 10^{-2}$ mol/L)

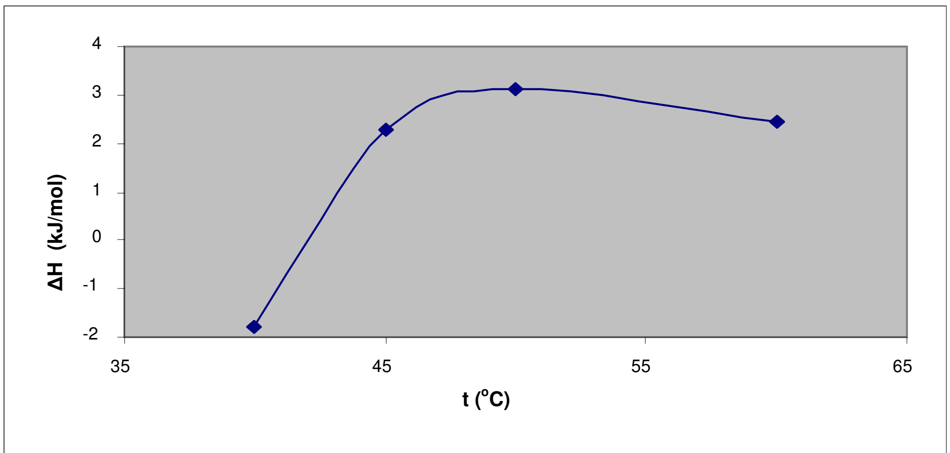

Figure C. 40: $\Delta H = f$ (t˚C) Curve of 1×10^{-3}(mol/L) PSP - 1×10^{-3}(mol/L) Na_2SO_4, ($I = 1 \times 10^{-2}$ mol/L)

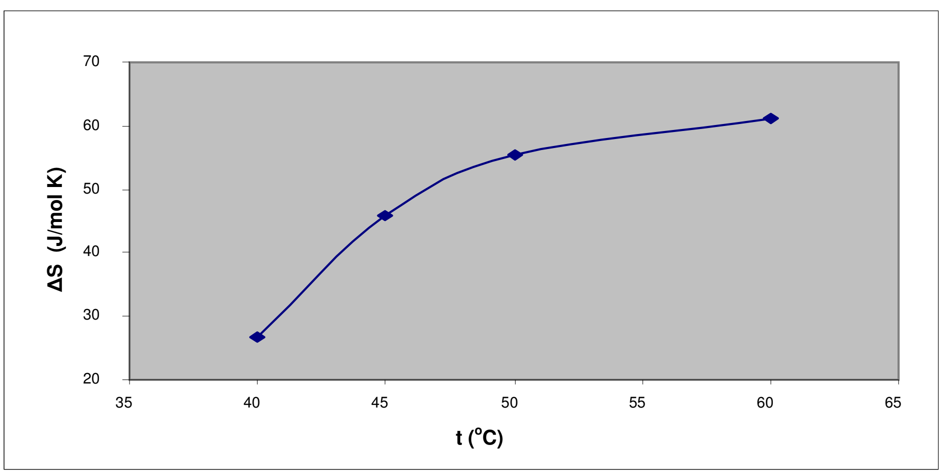

Figure C. 41: $\Delta S = f$ (t˚C) Curve of 1×10^{-3}(mol/L) PSP-1×10^{-3}(mol/L) Na_2SO_4, ($I = 1 \times 10^{-2}$ mol/L)

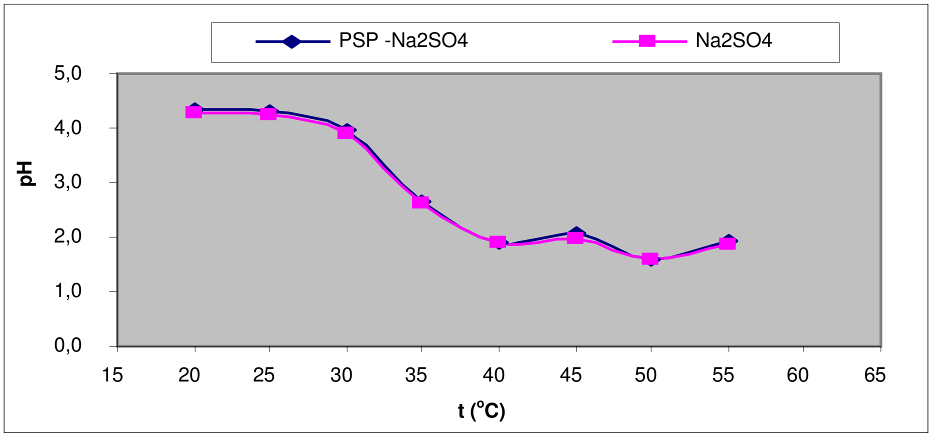

Figure C. 42: pH=f (t°C) Curve of 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) Na_2SO_4, (I=1x10^{-3} mol/L)

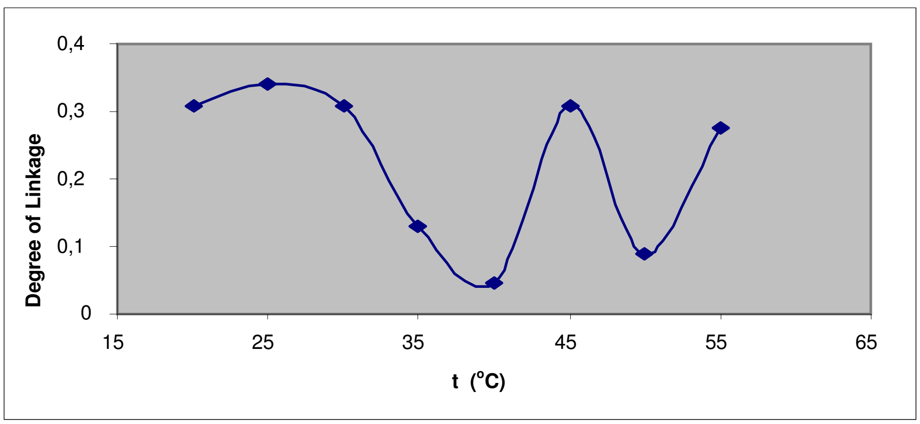

Figure C. 43: Degree of linkage, θ =f (t°C) Curve 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) Na_2SO_4, (I=1x10^{-3} mol/L)

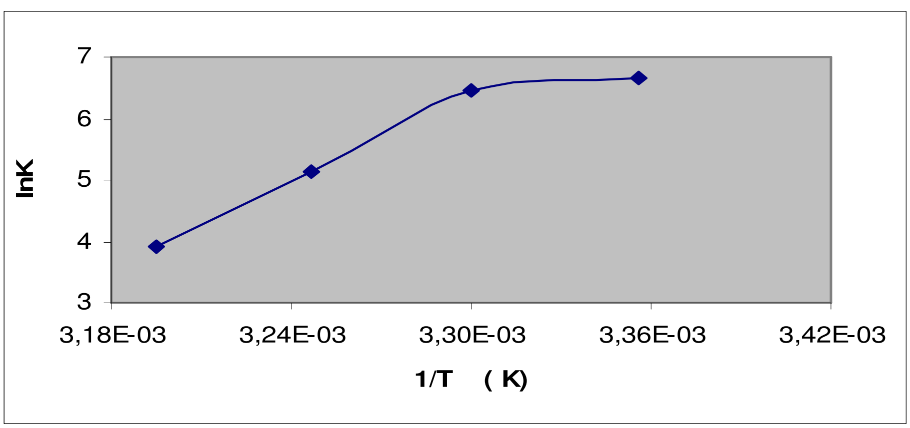

Figure C. 44: Curve of equilibrium constant 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) Na_2SO_4, (I=1x10^{-3} mol/L)

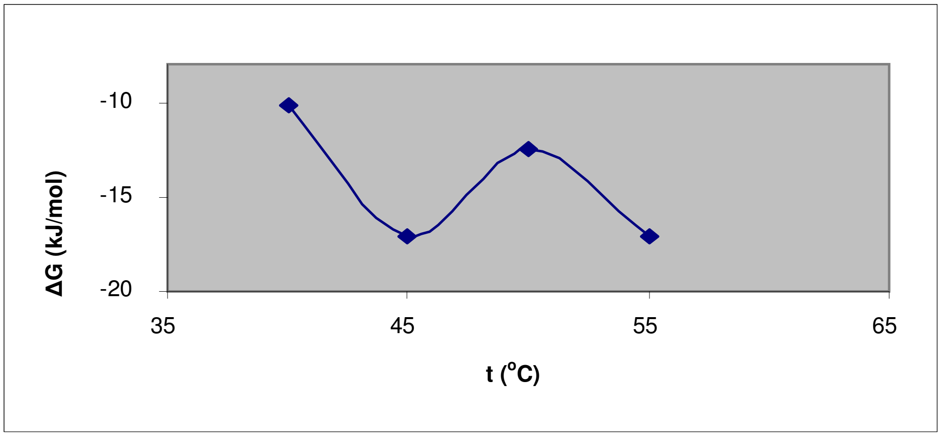

Figure C. 45: $\Delta G=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) Na_2SO_4, ($I=1x10^{-3}$ mol/L)

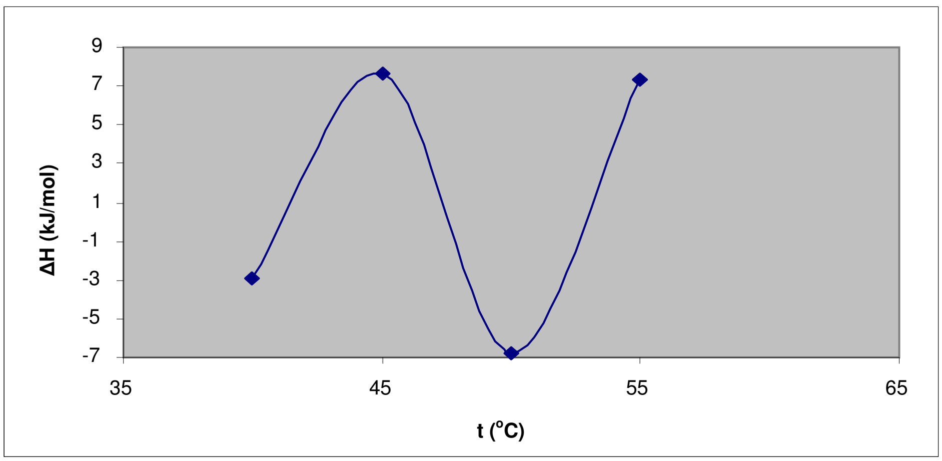

Figure C. 46: $\Delta H=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) Na_2SO_4, ($I=1x10^{-3}$ mol/L)

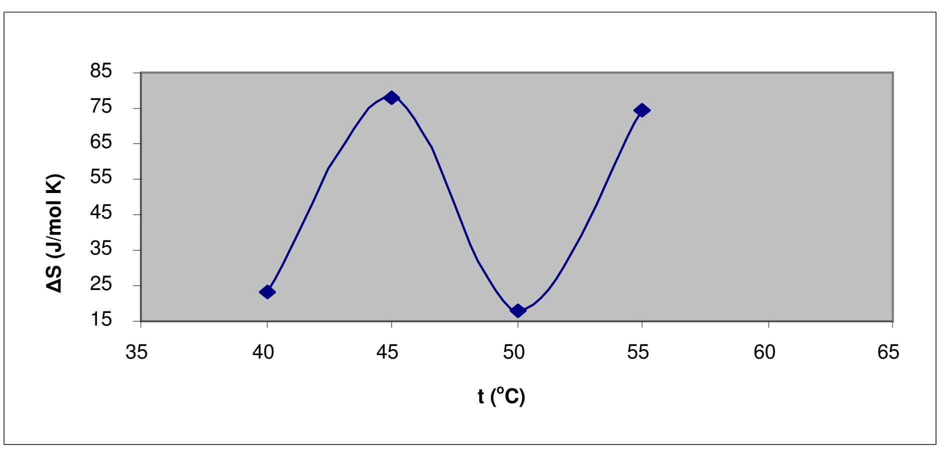

Figure C. 47: $\Delta S=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) Na_2SO_4, ($I=1x10^{-3}$ mol/L)

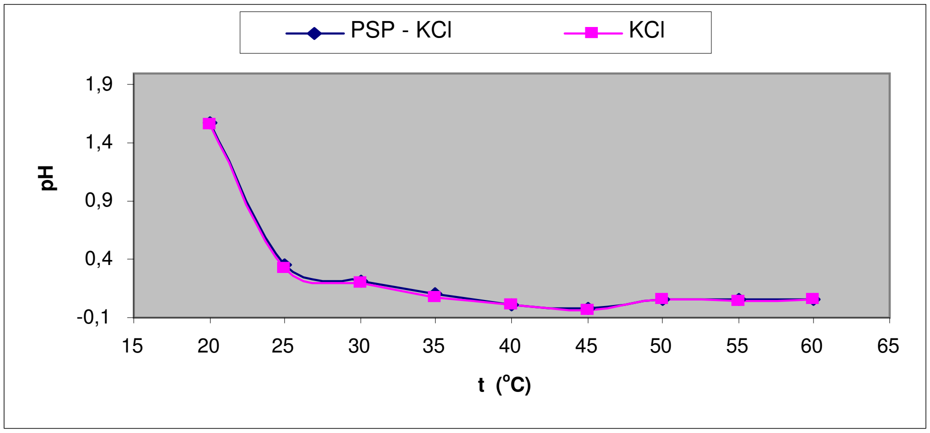

Figure C. 48: pH=*f* (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

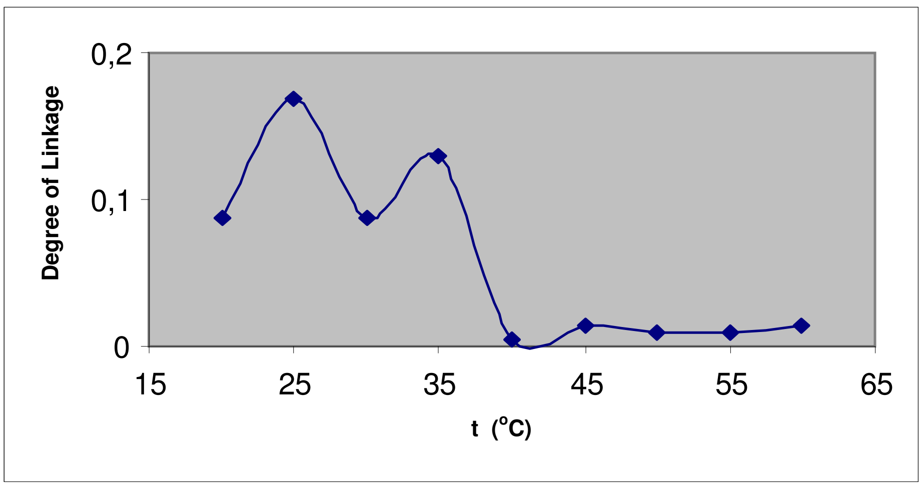

Figure C. 49: Degree of linkage, θ =*f* (t°C) Curve $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

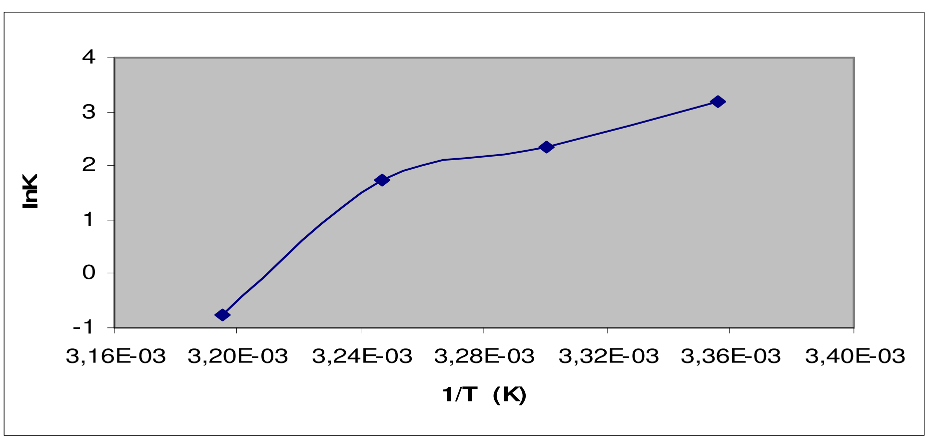

Figure C. 50: Curve of equilibrium constant $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

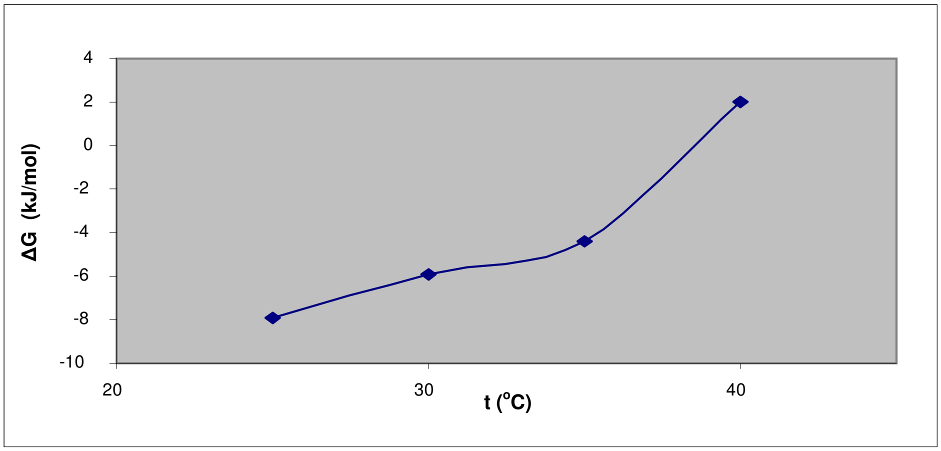

Figure C. 51: $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

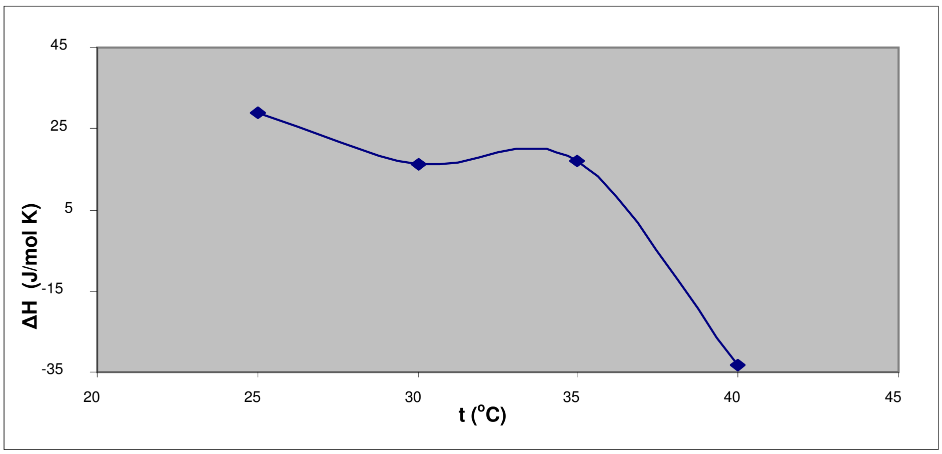

Figure C. 52: $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

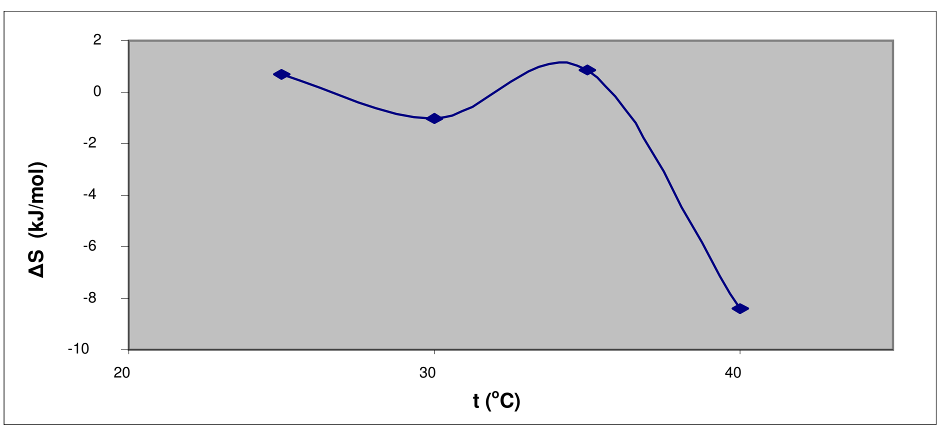

Figure C. 53: $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

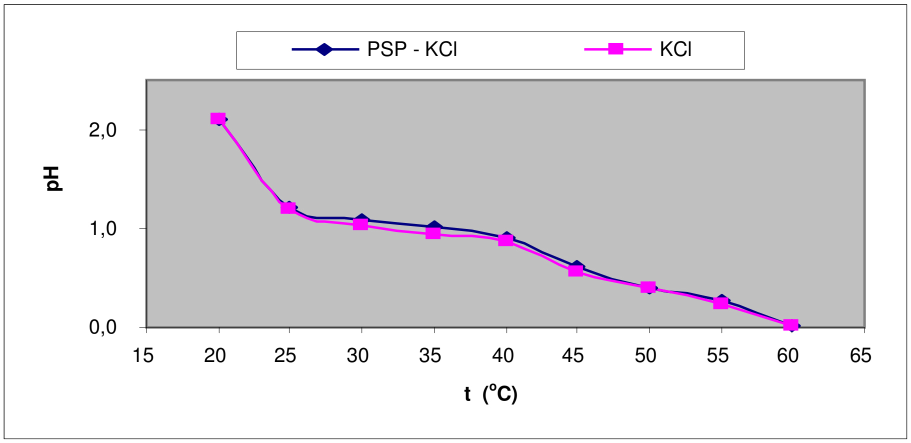

Figure C. 54: pH=f (t°C) Curve of $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

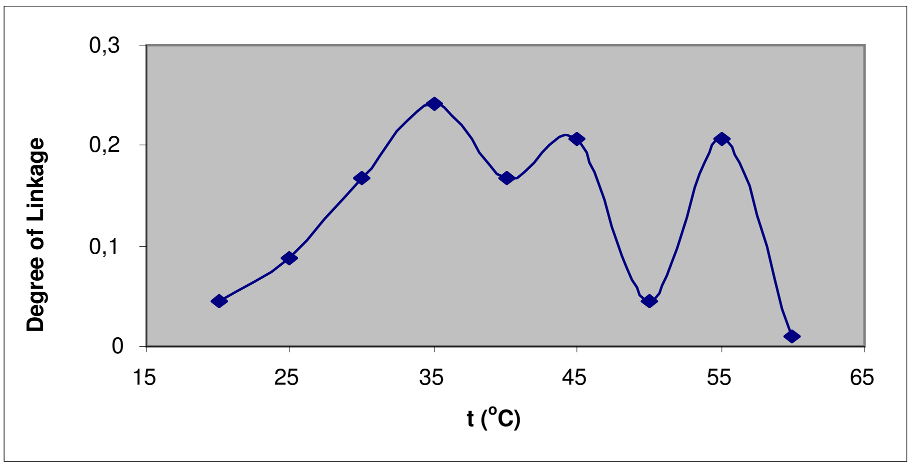

Figure C. 55: Degree of linkage, $\theta = f$ (t°C) Curve $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

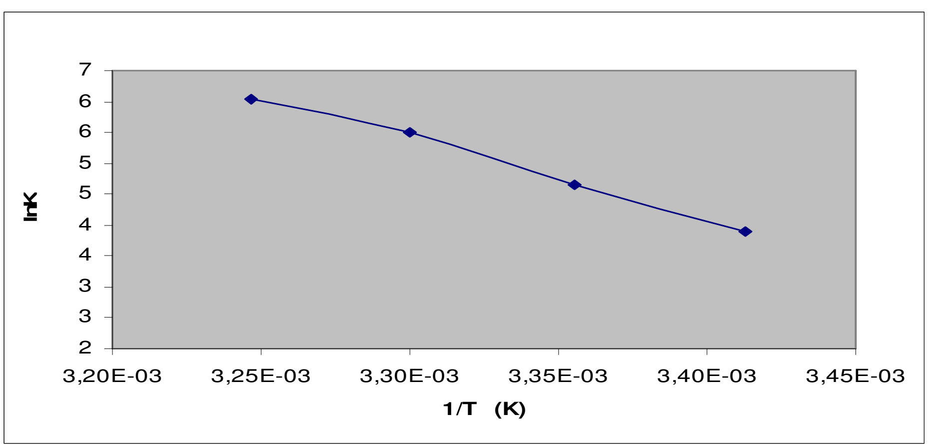

Figure C. 56: Curve of equilibrium constant $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

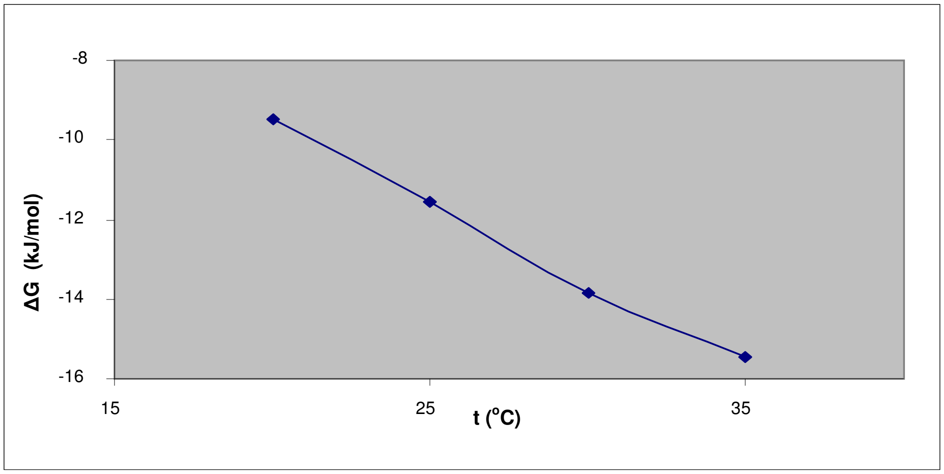

Figure C. 57: $\Delta G = f\,(t^{\circ}C)$ Curve of $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

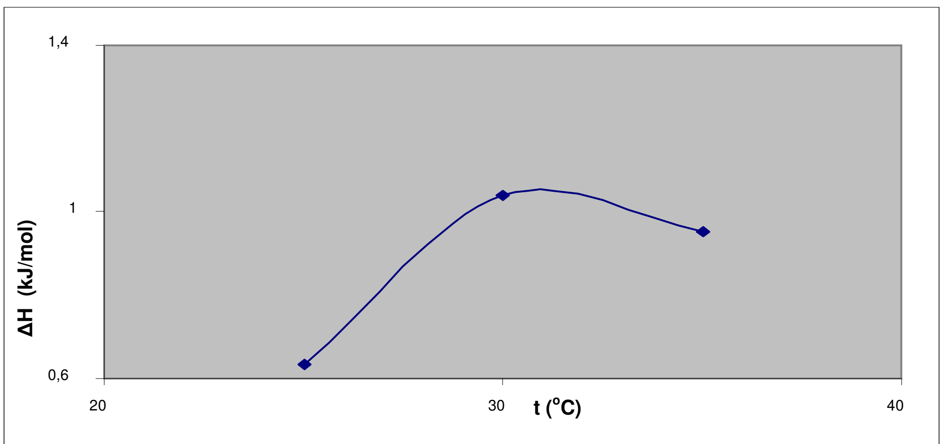

Figure C. 58: $\Delta H = f\,(t^{\circ}C)$ Curve of $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

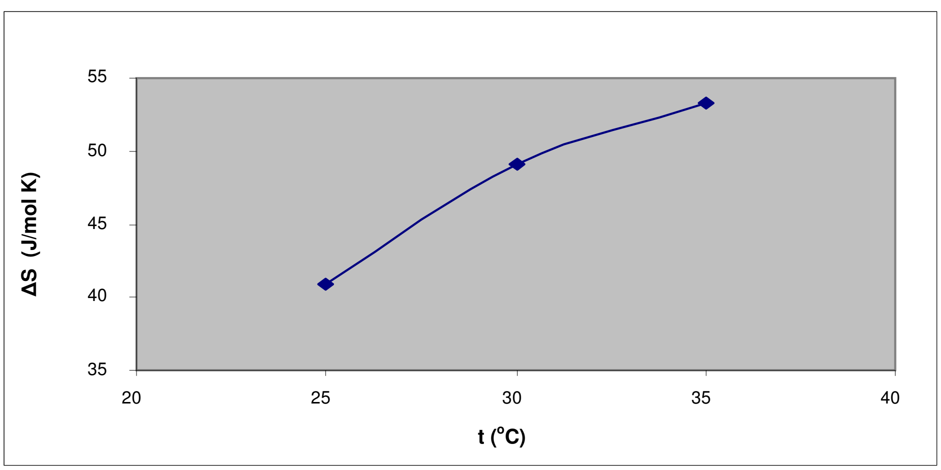

Figure C. 59: $\Delta S = f\,(t^{\circ}C)$ Curve of $1x10^{-3}$ (mol/L) PSP- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

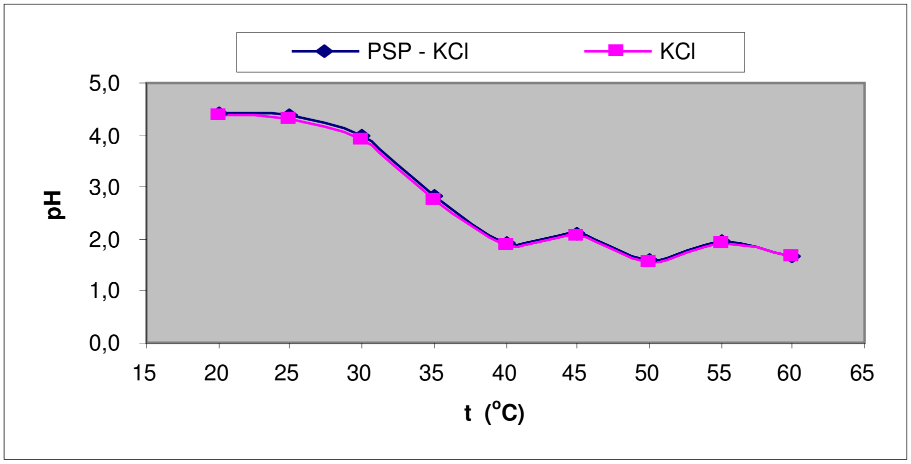

Figure C.2: pH=f (t°C) Curve of 1x10^{-4}(mol/L) PSP - 1x10^{-4}(mol/L) KCl, (I=1x10^{-3} mol/L)

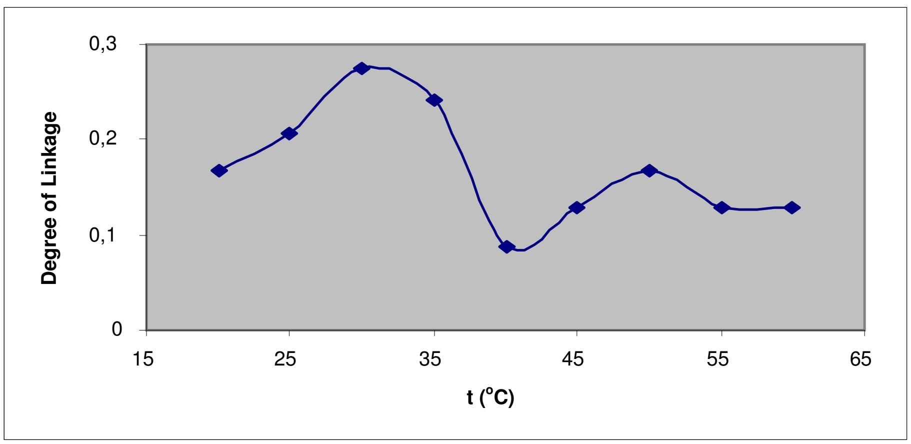

Figure C. 60: Degree of linkage, θ =f (t°C) Curve1x10^{-4}(mol/L) PSP-1x10^{-4}(mol/L) KCl, (I=1x10^{-3} mol/L)

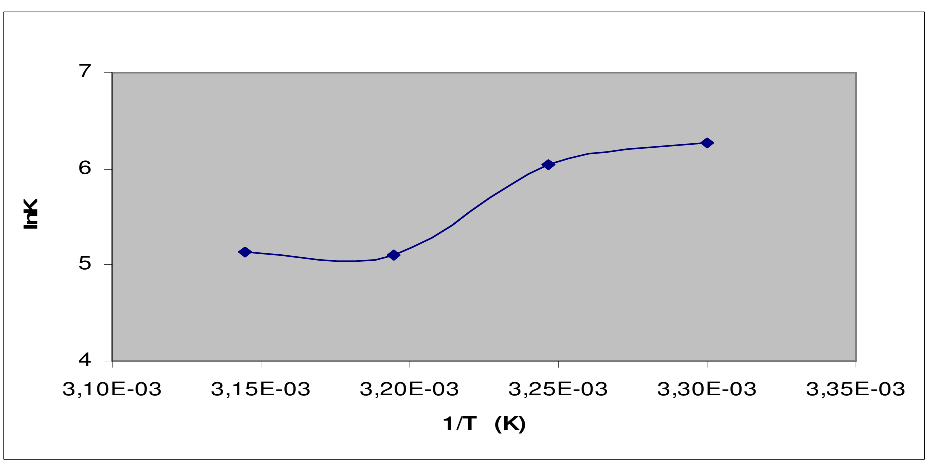

Figure C. 61: Curve of equilibrium constant 1x10^{-4}(mol/L) PSP-1x10^{-4}(mol/L) KCl, (I=1x10^{-3} mol/L)

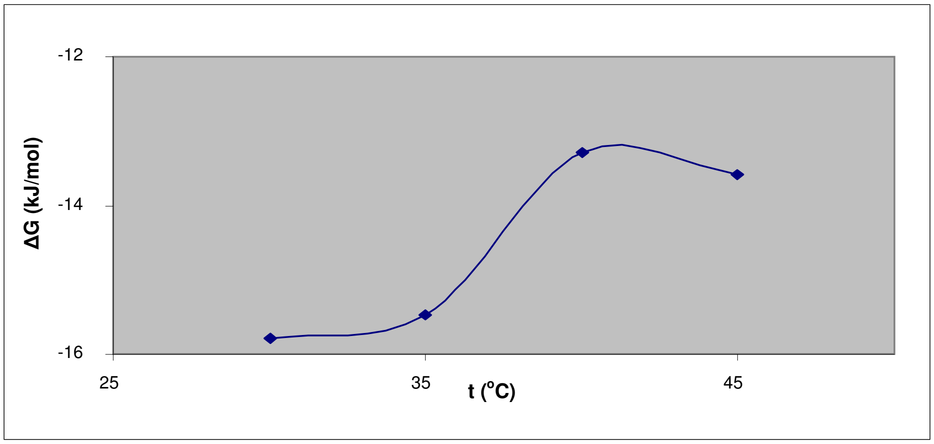

Figure C. 62: $\Delta G = f\ (t^{\circ}C)$ Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) KCl, ($I=1x10^{-3}$ mol/L)

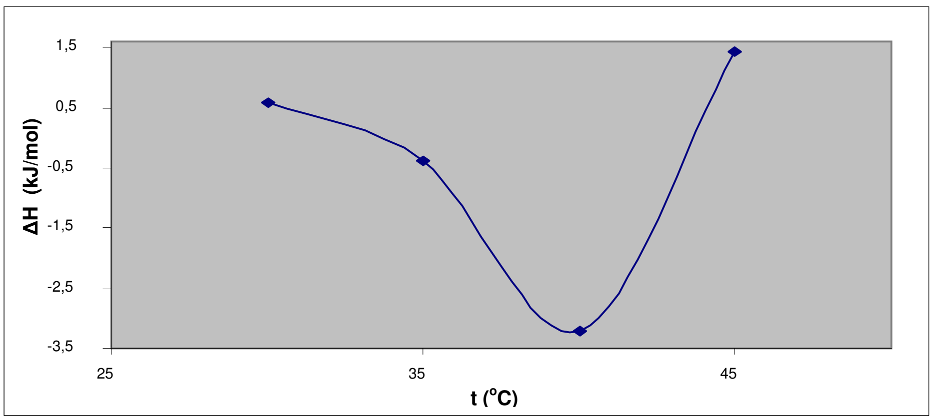

Figure C. 63: $\Delta H = f\ (t^{\circ}C)$ Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) KCl, ($I=1x10^{-3}$ mol/L)

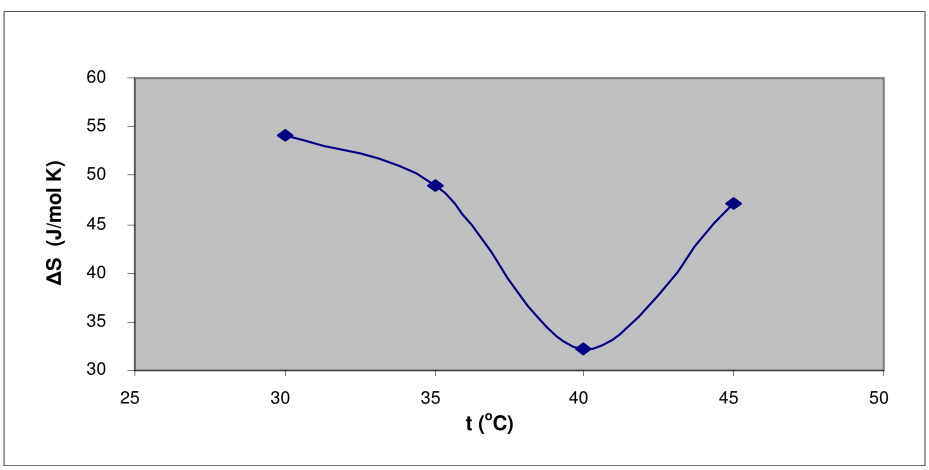

Figure C. 64: $\Delta S = f\ (t^{\circ}C)$ Curve of $1x10^{-4}$(mol/L) PSP - $1x10^{-4}$(mol/L) KCl, ($I=1x10^{-3}$ mol/L)

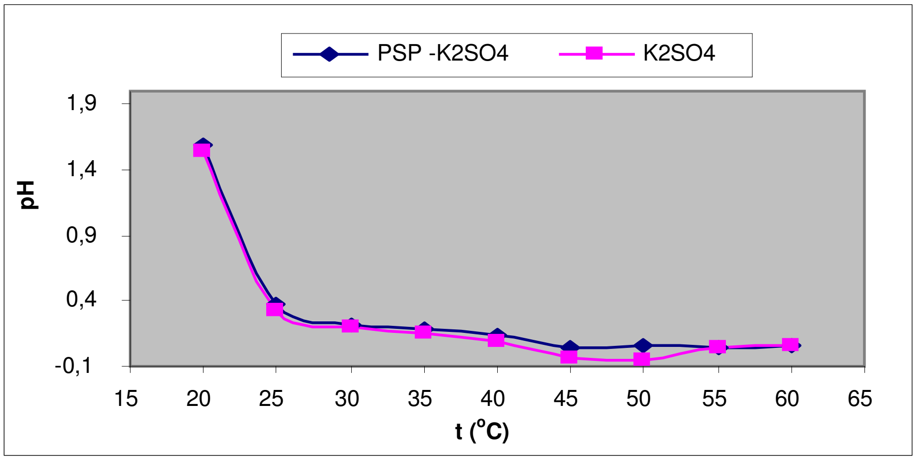

Figure C.3: pH=f (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) K_2SO_4, (I=$1x10^{-1}$ mol/L)

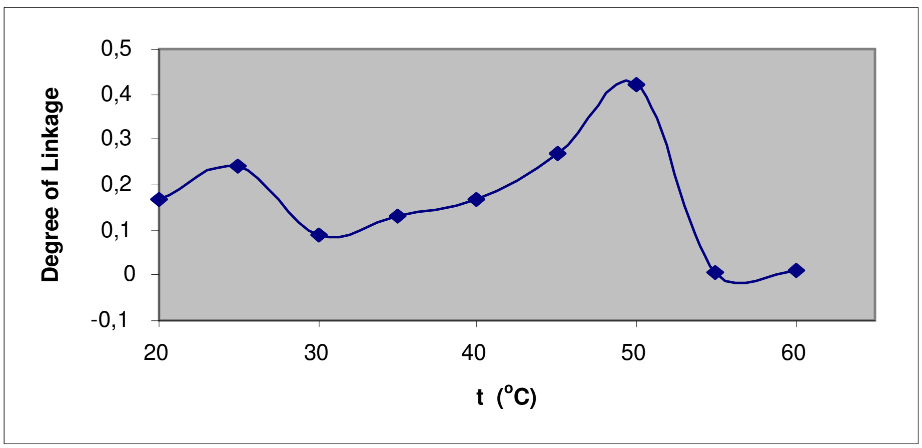

Figure C. 65: Degree of linkage, θ =f (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L)K_2SO_4,(I=$1x10^{-1}$ mol/L)

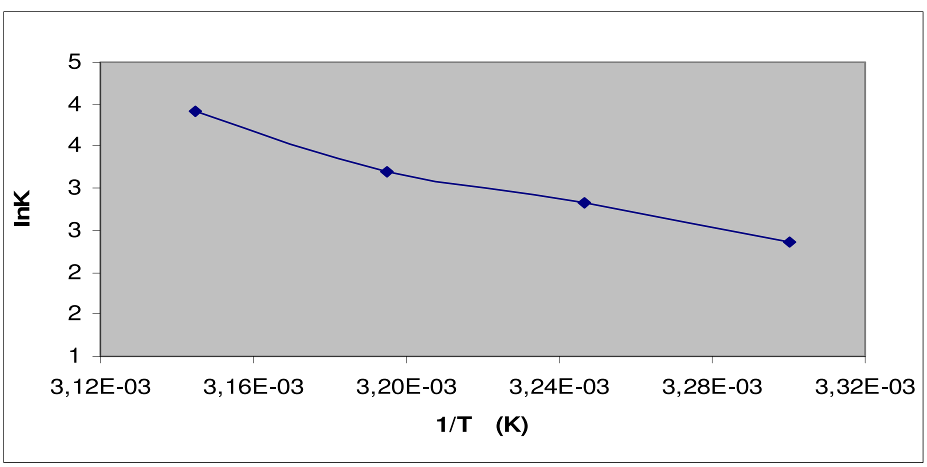

Figure C. 66: Curve of equilibrium constant $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) K_2SO_4, (I=$1x10^{-1}$ mol/L)

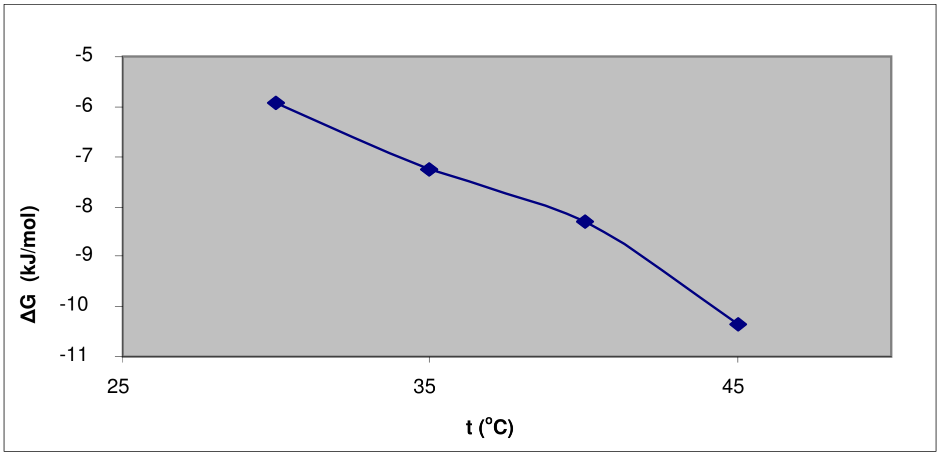

Figure C. 67: $\Delta G = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

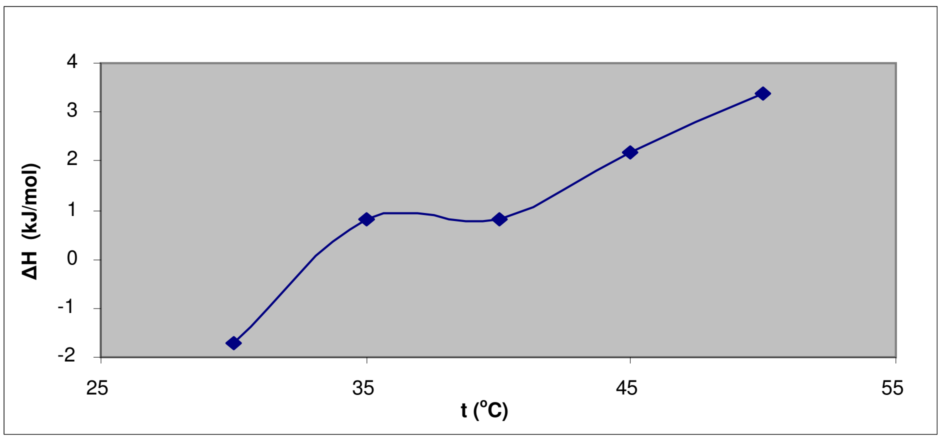

Figure C. 68: $\Delta H = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

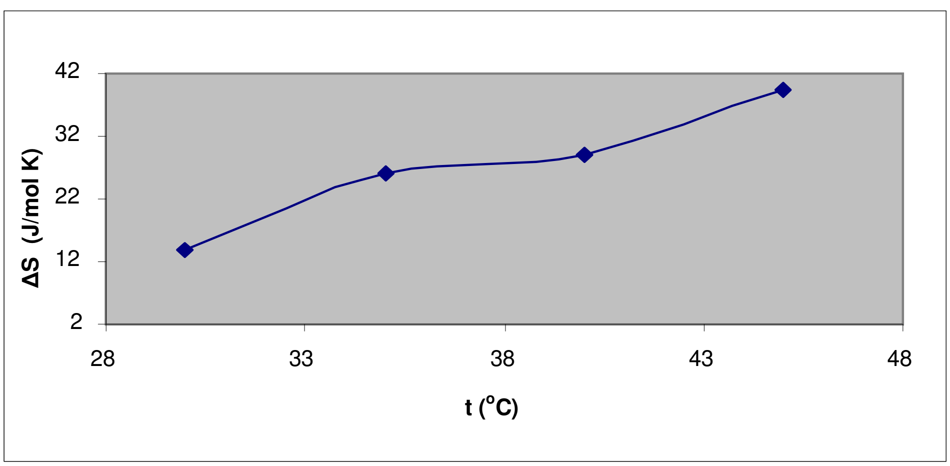

Figure C. 69: $\Delta S = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

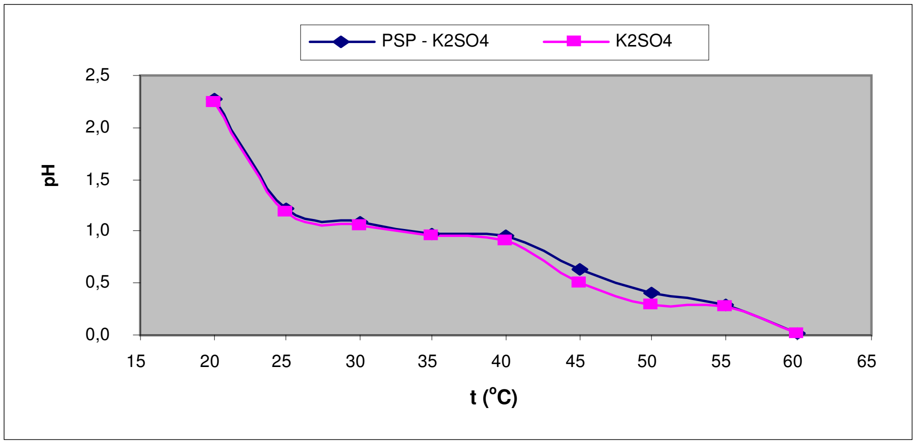

Figure C.4: pH=f (t°C) Curve of of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

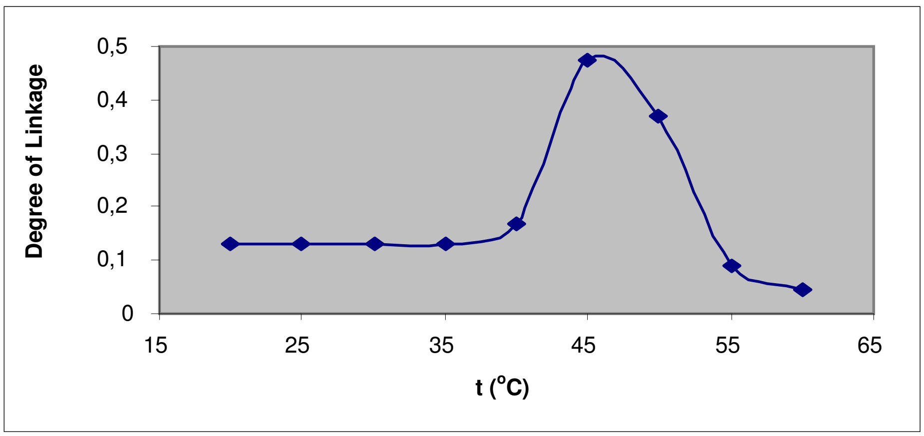

Figure C. 70: Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

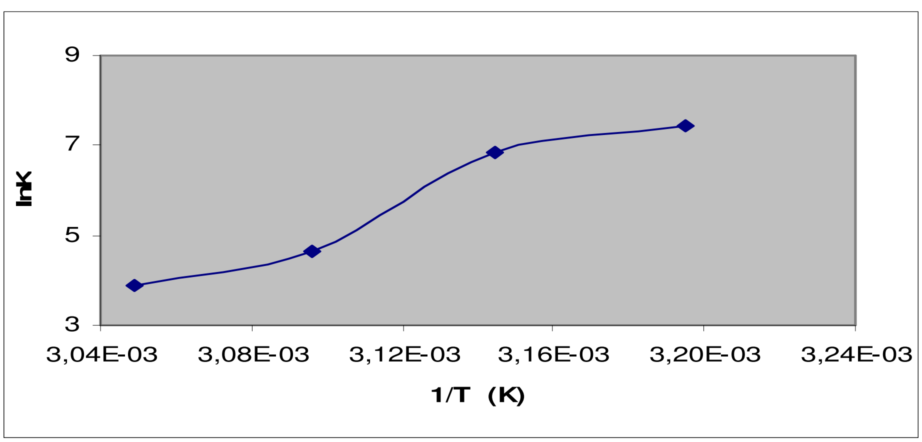

Figure C. 71: Curve of equilibrium constant $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

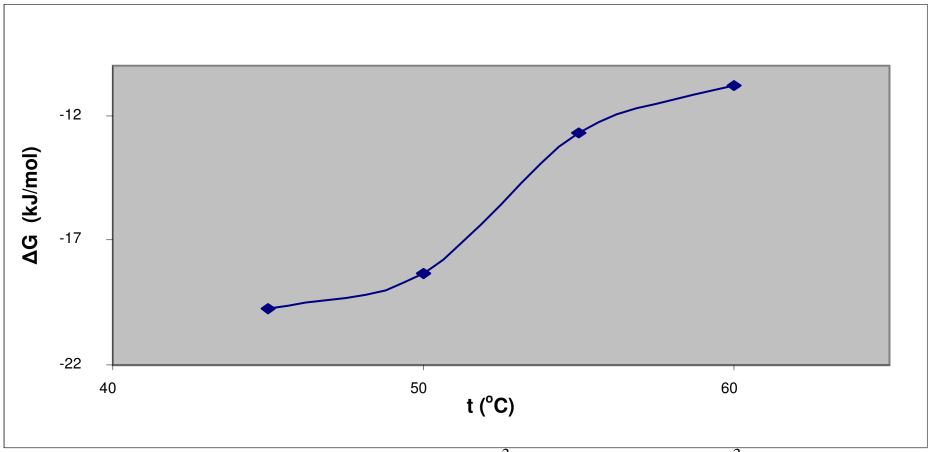

Figure C. 72: ΔG=*f* (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

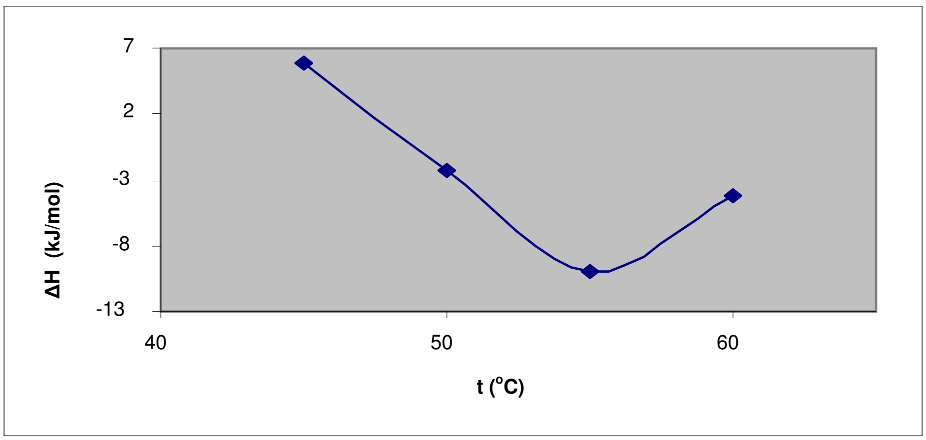

Figure C. 73: ΔH=*f* (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

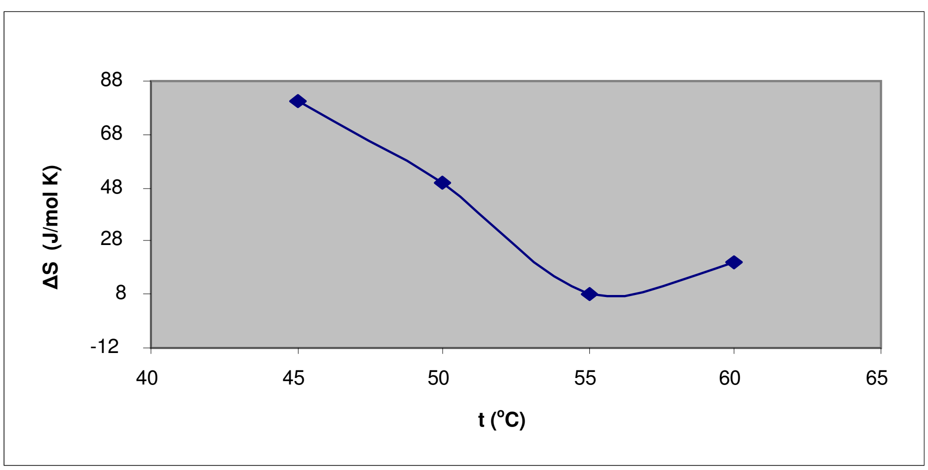

Figure C. 74: ΔS=*f* (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) K_2SO_4 (I=$1x10^{-2}$ mol/L)

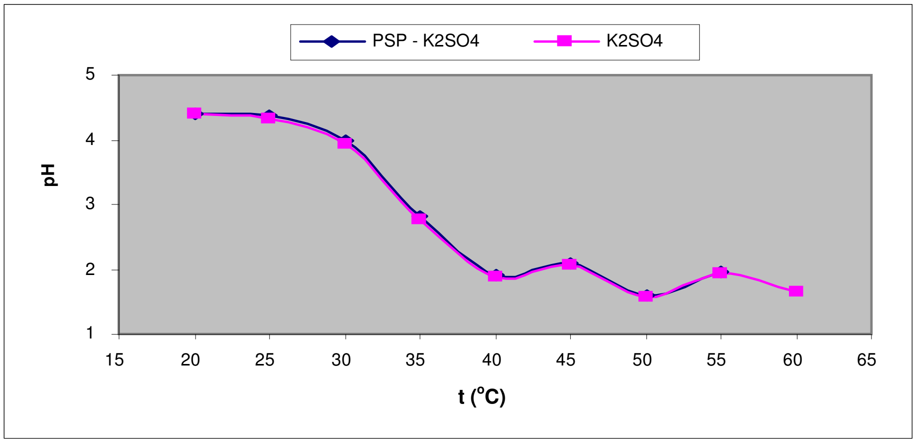

Figure C. 75: pH=f (t°C) Curve of 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) K_2SO_4 (I=1x10^{-3} mol/L)

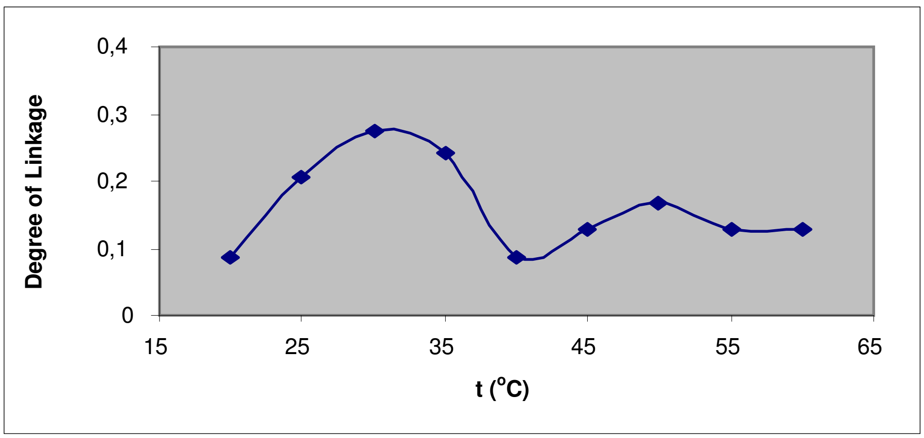

Figure C. 76: Degree of linkage, $\theta = f$ (t°C) Curve of 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) K_2SO_4, (I=1x10^{-3} mol/L)

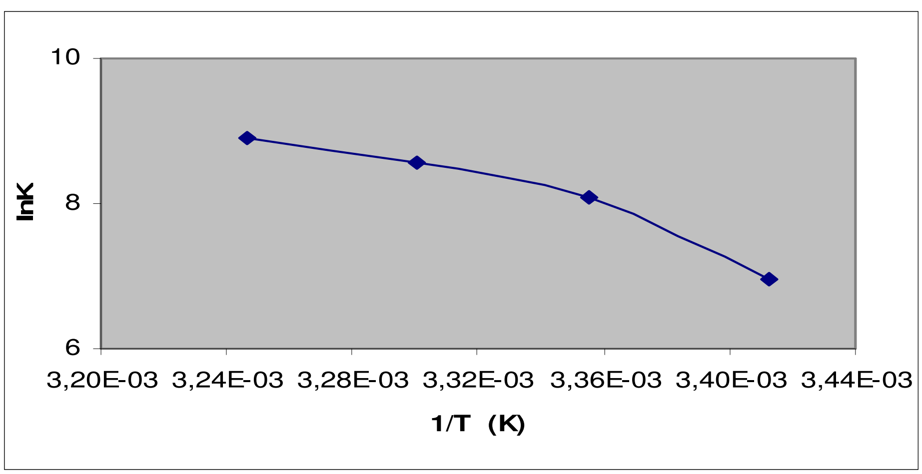

Figure C. 77: Curve of equilibrium constant 1x10^{-4}(mol/L) PSP- 1x10^{-4}(mol/L) K_2SO_4 (I=1x10^{-3} mol/L)

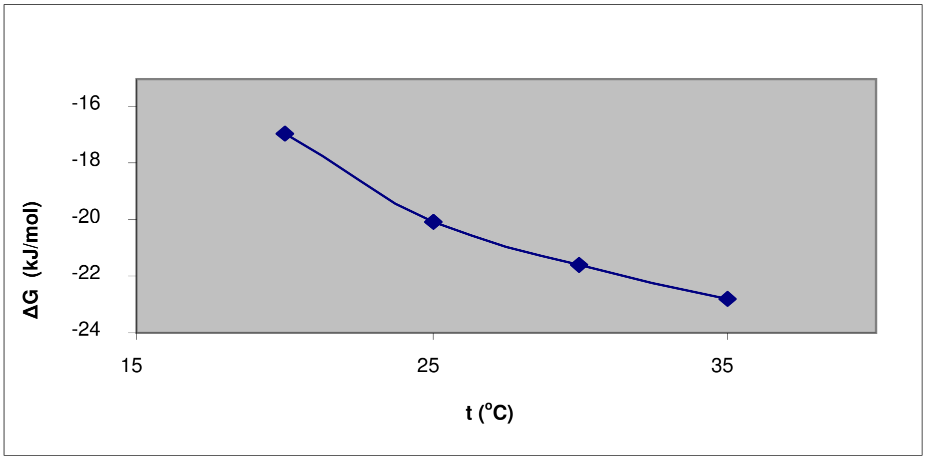

Figure C. 78: $\Delta G = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) K_2SO_4 ($I=1x10^{-3}$ mol/L)

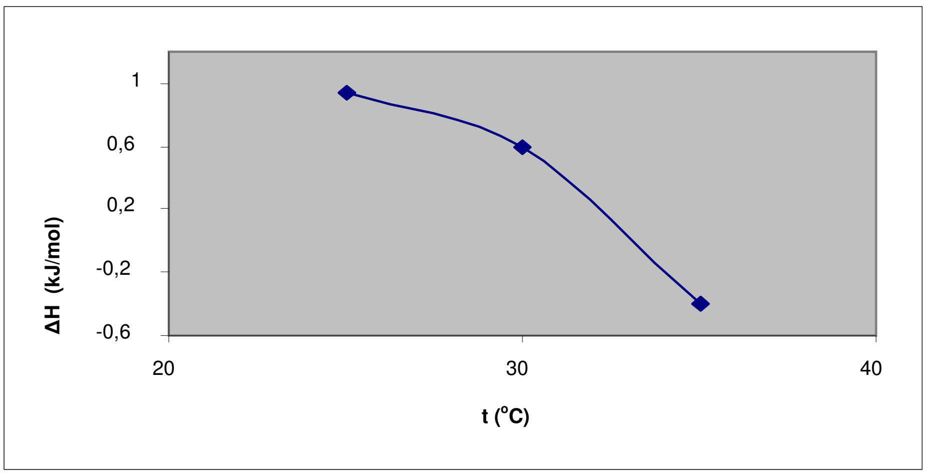

Figure C. 79: $\Delta H = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) K_2SO_4 ($I=1x10^{-3}$ mol/L)

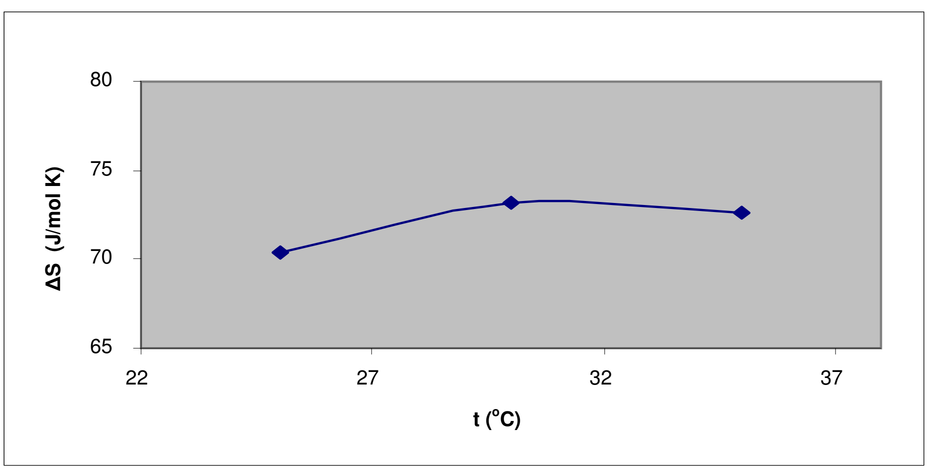

Figure C. 80: $\Delta S = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) K_2SO_4 ($I=1x10^{-3}$ mol/L)

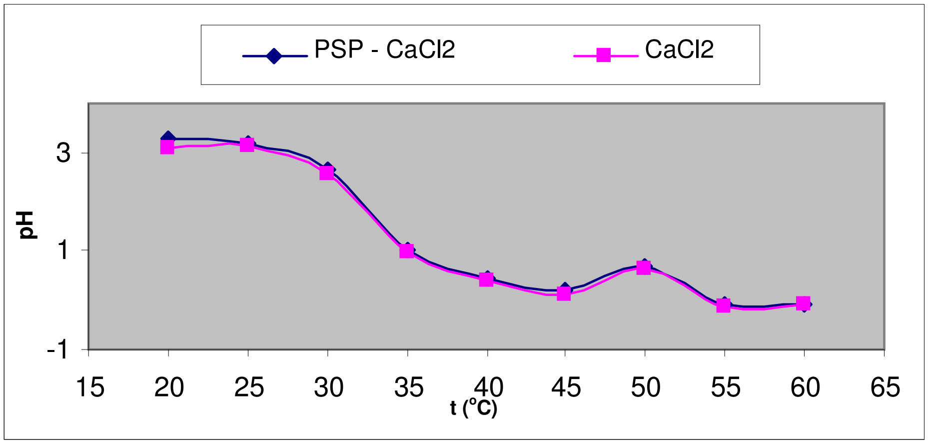

Figure C. 81: pH=*f* (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

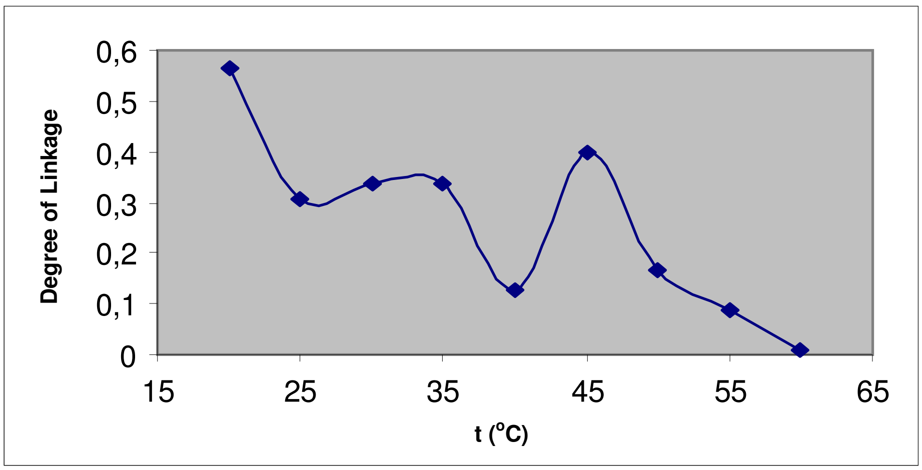

Figure C. 82: Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

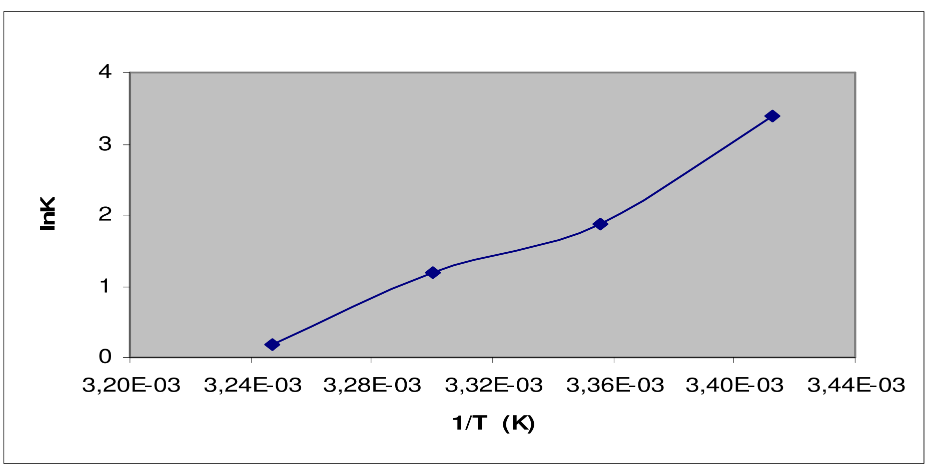

Figure C. 83: Curve of equilibrium constant $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

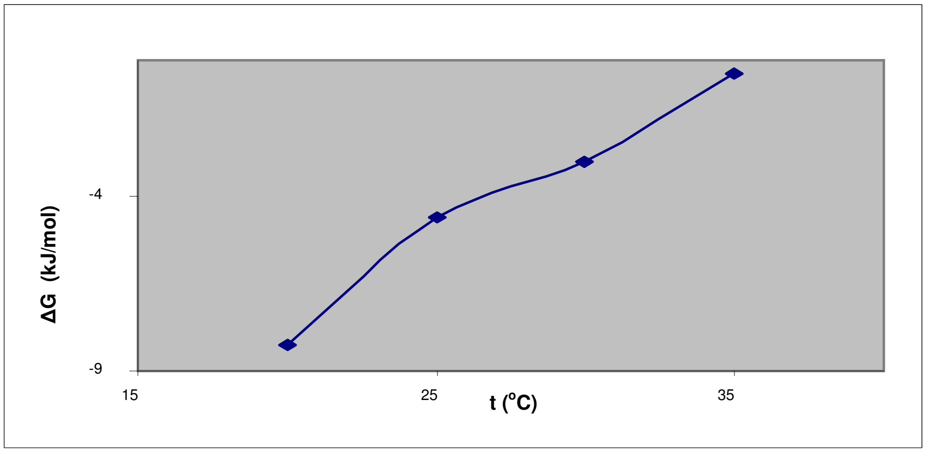

Figure C. 84: $\Delta G = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

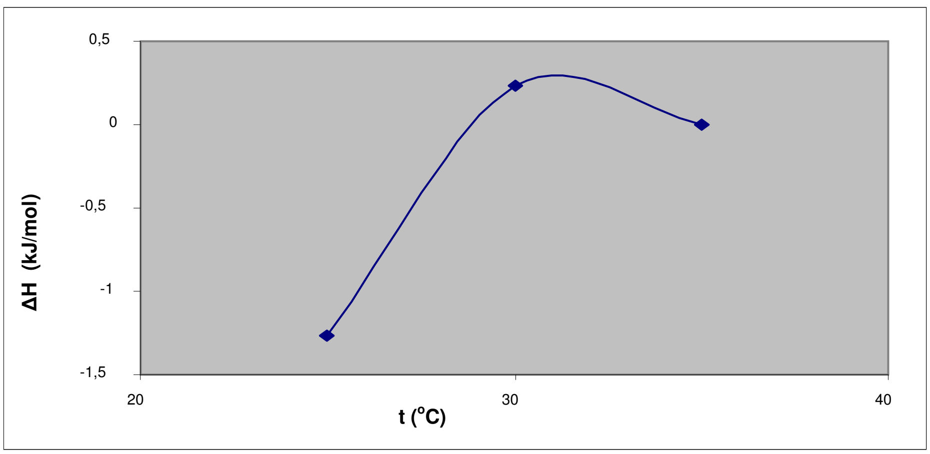

Figure C. 85: $\Delta H = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

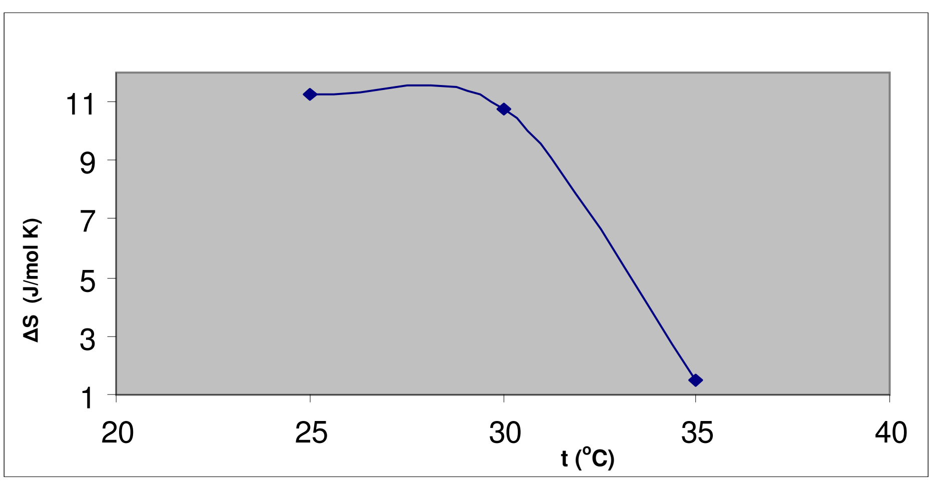

Figure C. 86: $\Delta S = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PSP- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

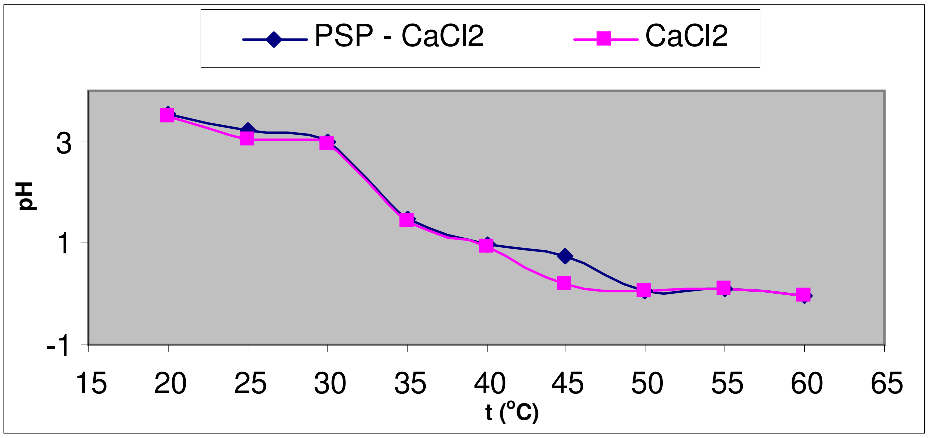

Figure C. 87: pH=f (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) $CaCl_2$, ($I=1x10^{-1}$ mol/L)

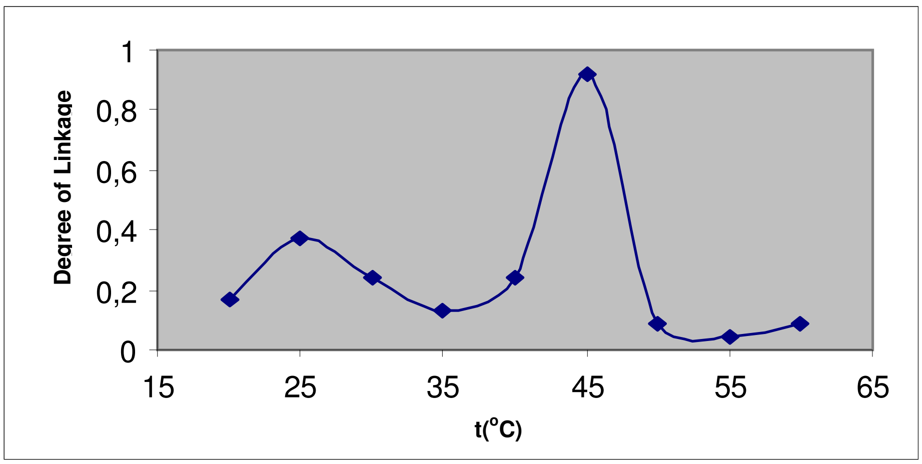

Figure C. 88: Degree of linkage, θ =f (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L)$CaCl_2$ ($I=1x10^{-1}$ mol/L)

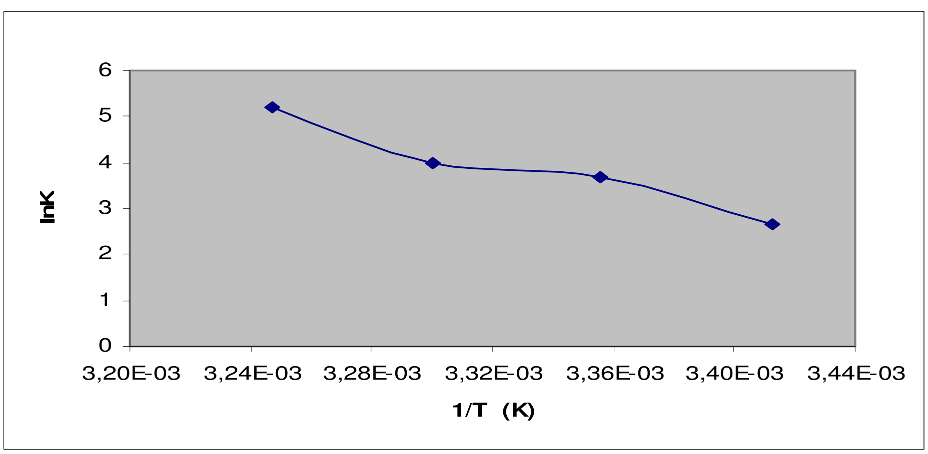

Figure C. 89: Curve of equilibrium constant $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) $CaCl_2$, ($I=1x10^{-1}$ mol/L)

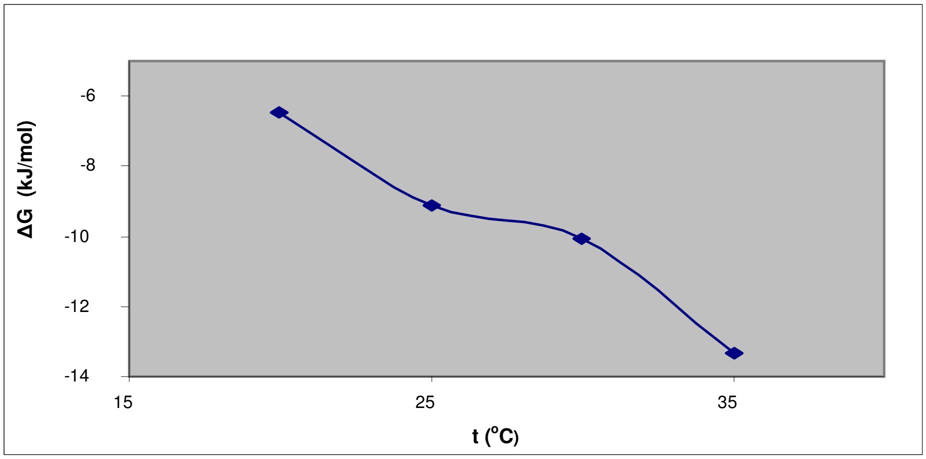

Figure C. 90: $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) $CaCl_2$ (I=$1x10^{-1}$ mol/L)

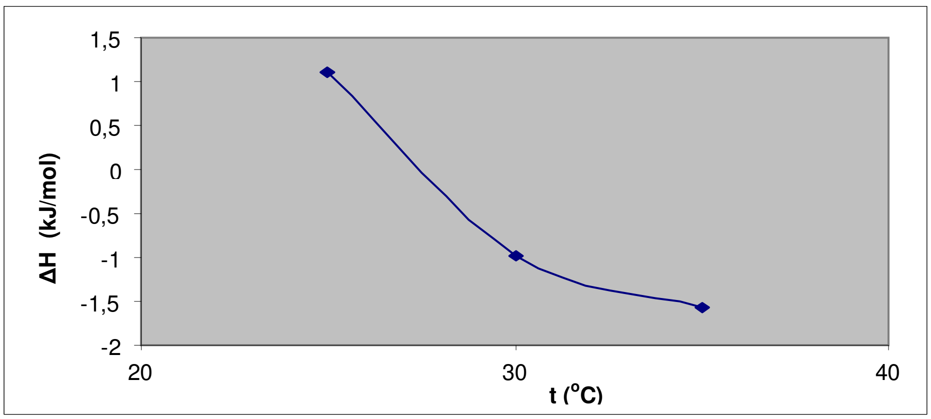

Figure C. 91: $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) $CaCl_2$ (I=$1x10^{-1}$ mol/L)

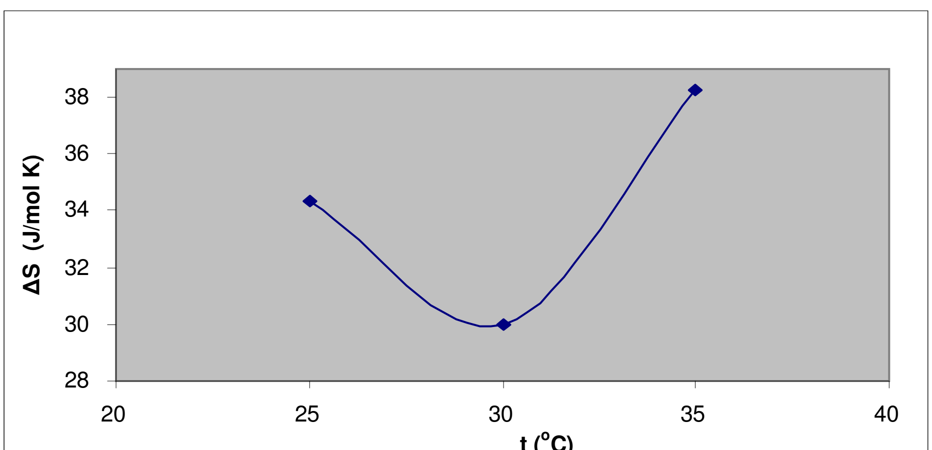

Figure C. 92: $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PSP- $1x10^{-2}$(mol/L) $CaCl_2$ (I=$1x10^{-1}$ mol/L)

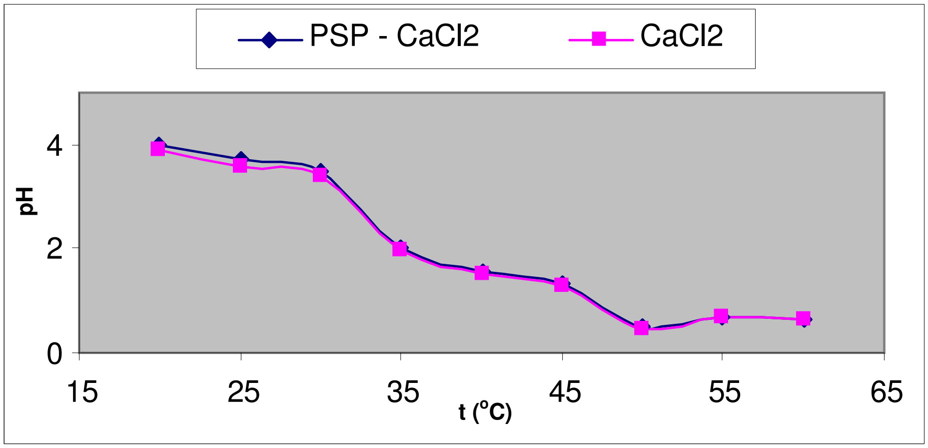

Figure C. 93: pH=f (t°C) Curve of 1x10^{-3}(mol/L) PSP- 1x10^{-3}(mol/L) $CaCl_2$ (I=1x10^{-2} mol/L)

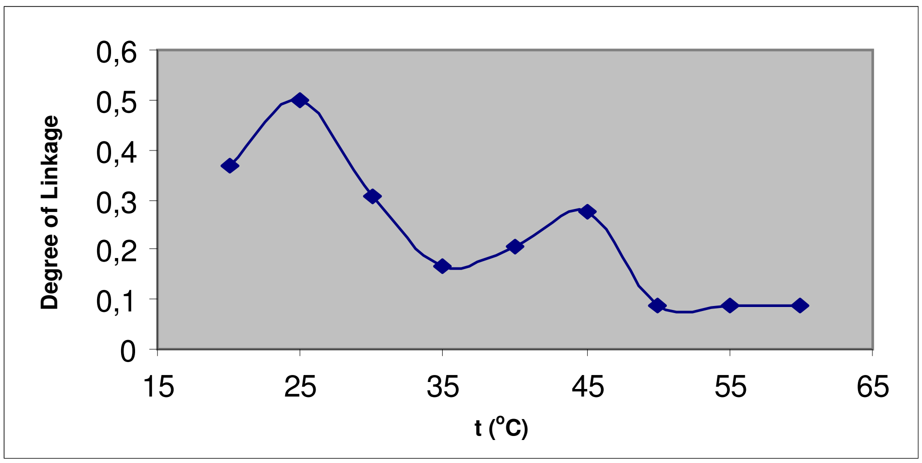

Figure C. 94: Degree of linkage, θ =f (t°C) Curve of 1x10^{-3}(mol/L) PSP- 1x10^{-3}(mol/L) $CaCl_2$ (I=1x10^{-2} mol/L)

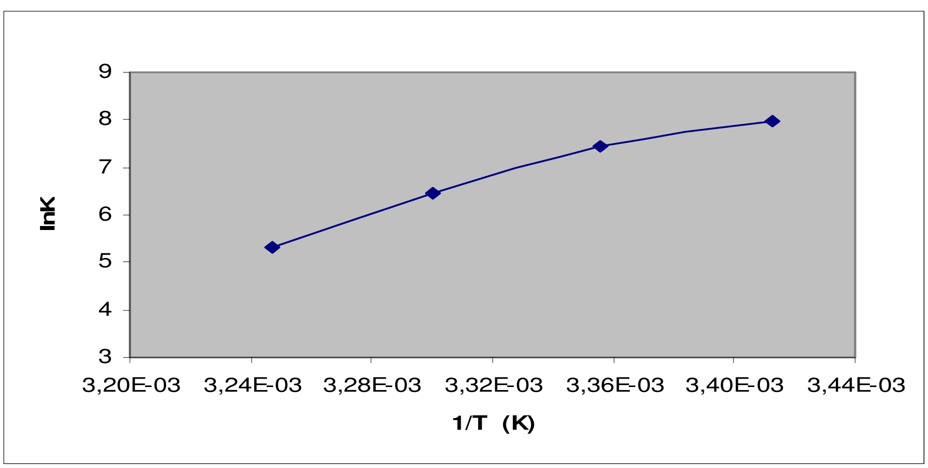

Figure C. 95: Curve of equilibrium constant 1x10^{-3}(mol/L) PSP- 1x10^{-3}(mol/L) $CaCl_2$ (I=1x10^{-2} mol/L)

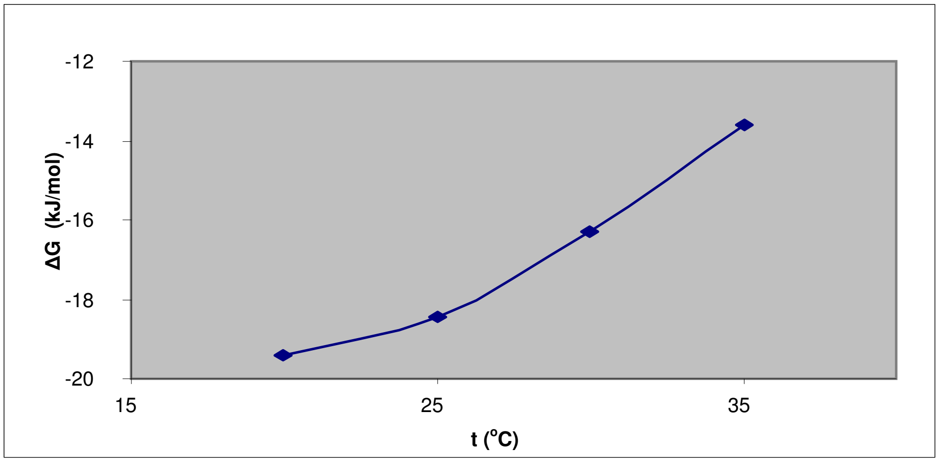

Figure C. 96: $\Delta G=f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) $CaCl_2$ ($I=1x10^{-2}$ mol/L)

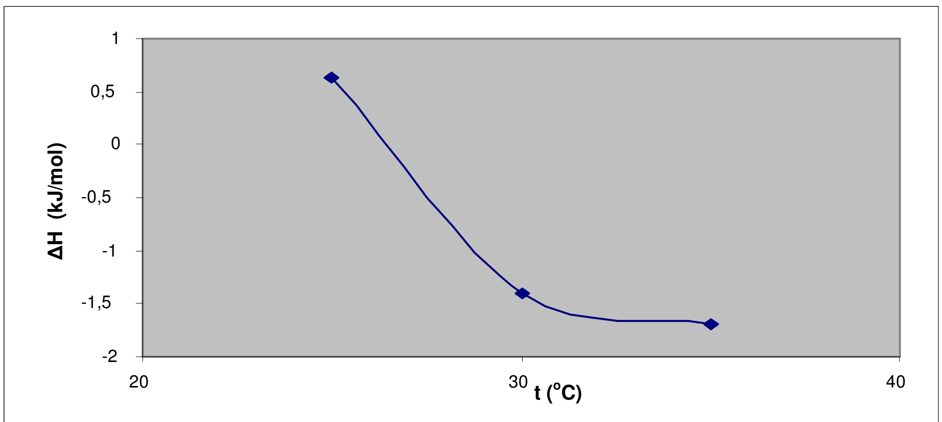

Figure C. 97: $\Delta H=f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) $CaCl_2$, ($I=1x10^{-2}$ mol/L)

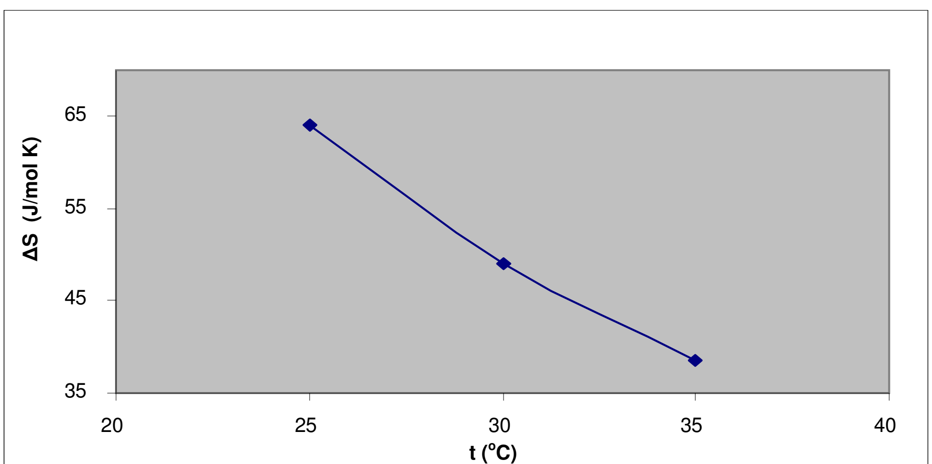

Figure C. 98: $\Delta S=f$ (t°C) Curve of $1x10^{-3}$(mol/L) PSP- $1x10^{-3}$(mol/L) $CaCl_2$ ($I=1x10^{-2}$ mol/L)

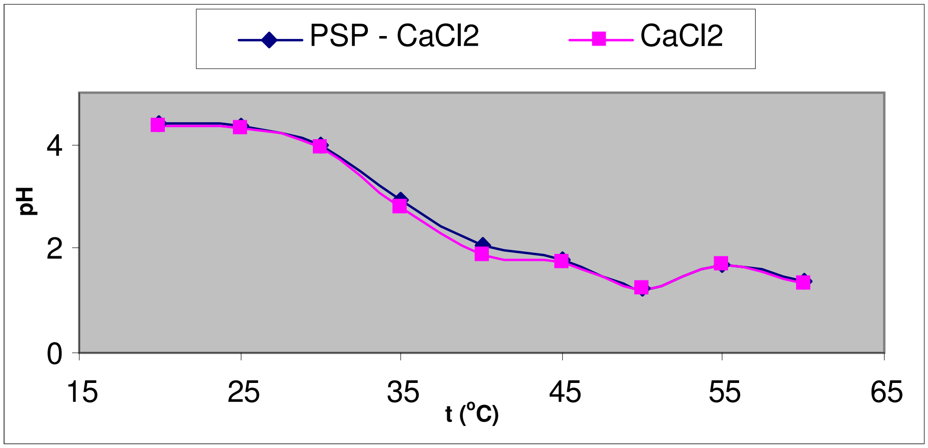

Figure C. 99: pH=f (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

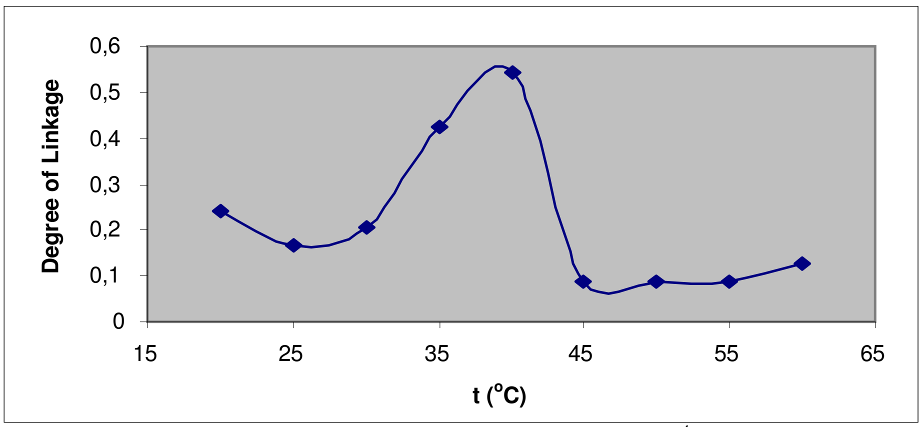

Figure C. 100: Degree of linkage, θ =f(t °C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

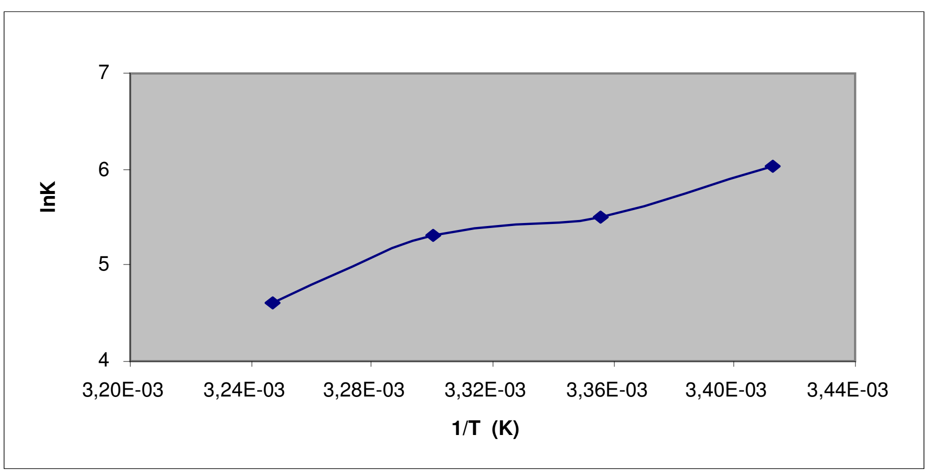

Figure C. 101: Curve of equilibrium constant $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

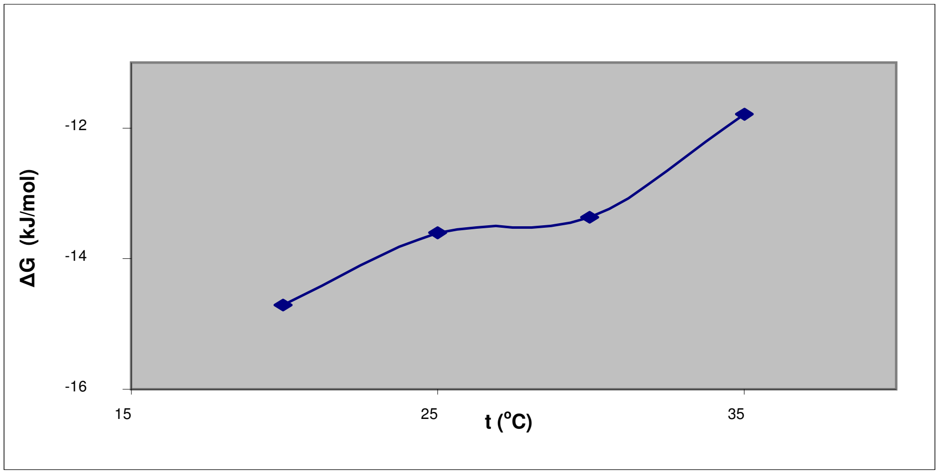

Figure C. 102: $\Delta G = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

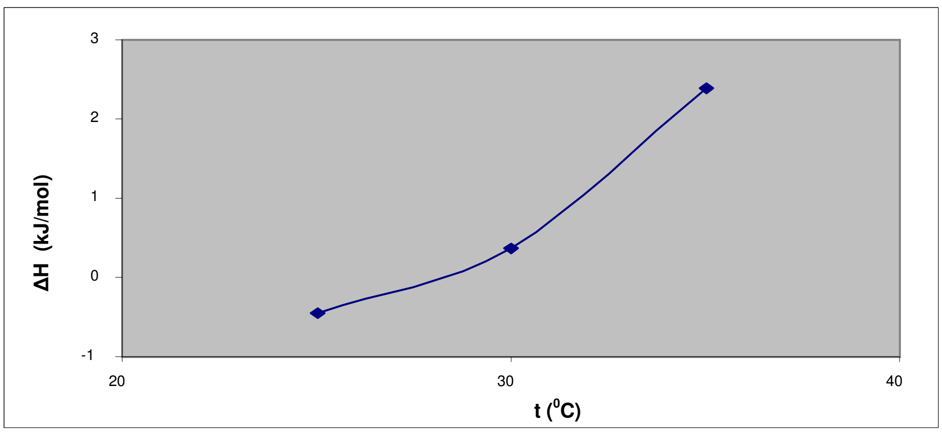

Figure C. 103: $\Delta H = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$ ($I=1x10^{-3}$ mol/L)

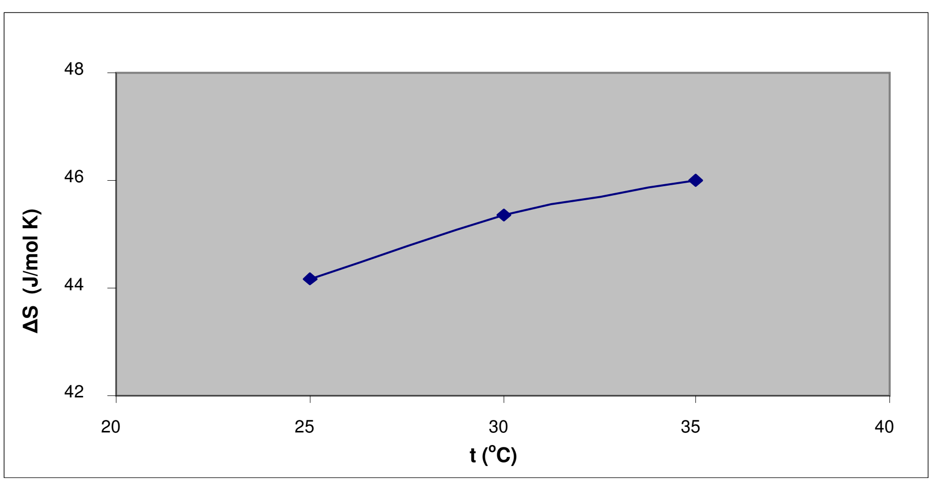

Figure C. 104: $\Delta S = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PSP- $1x10^{-4}$(mol/L) $CaCl_2$ ($I=1x10^{-3}$ mol/L)

APPENDIX D: Figures of Thermodynamic Results for PAH-Salt (I=constant)

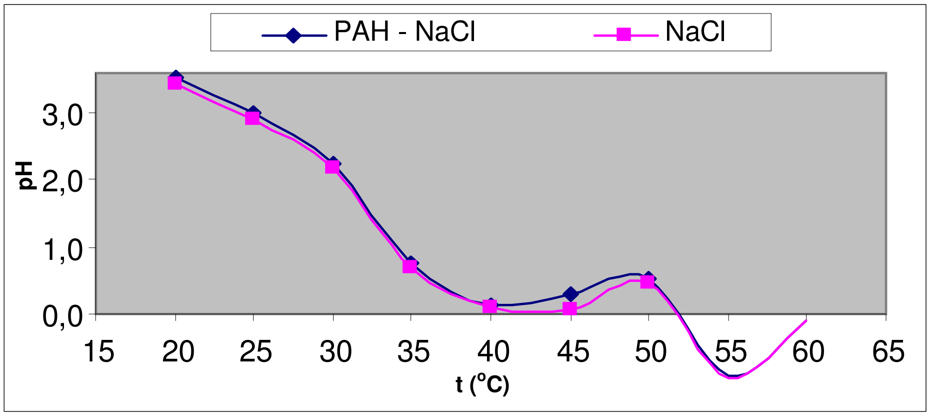

Figure D.1 : pH=f(t °C) Curve of $1x10^{-1}$(mol/L)PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

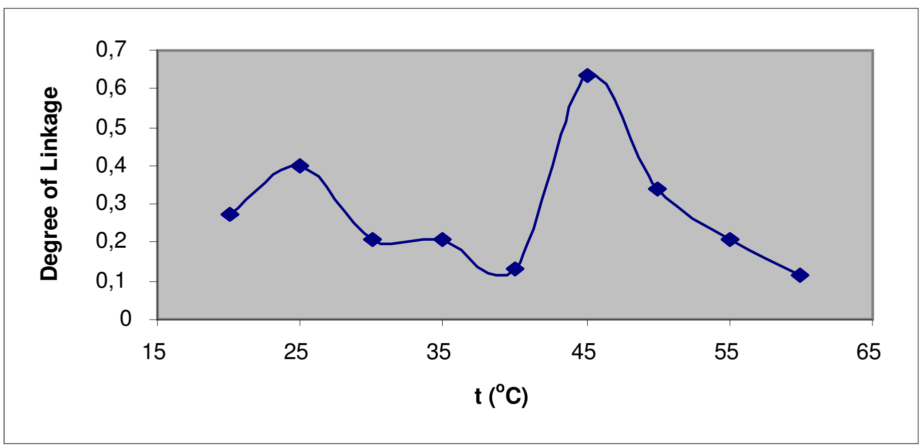

Figure D.2 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

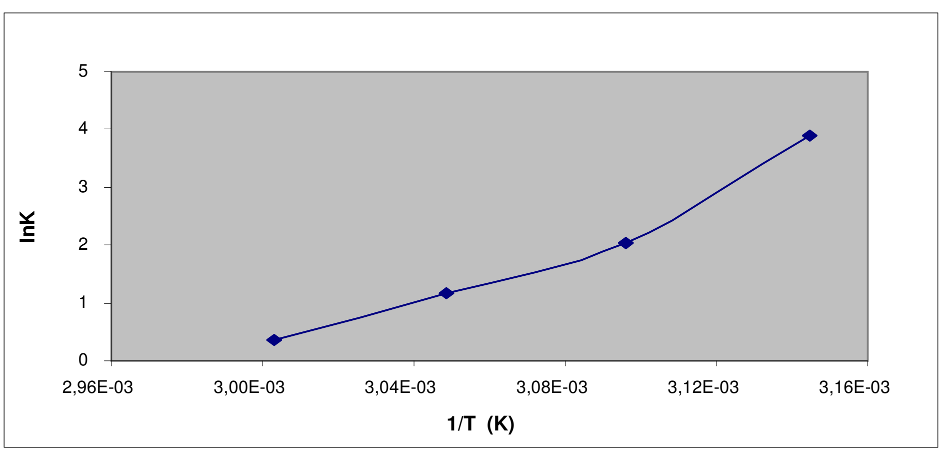

Figure D.3 : Curve of equilibrium constant $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

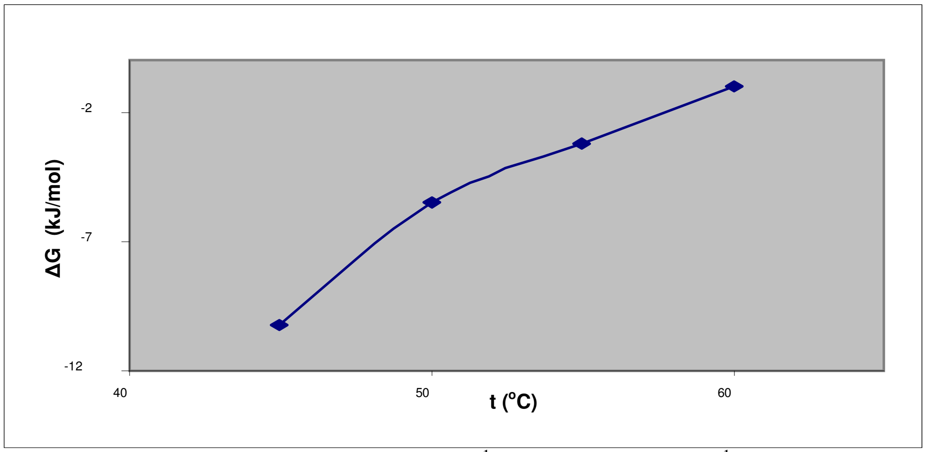

Figure D.4 : $\Delta G = f\,(t°C)$ Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

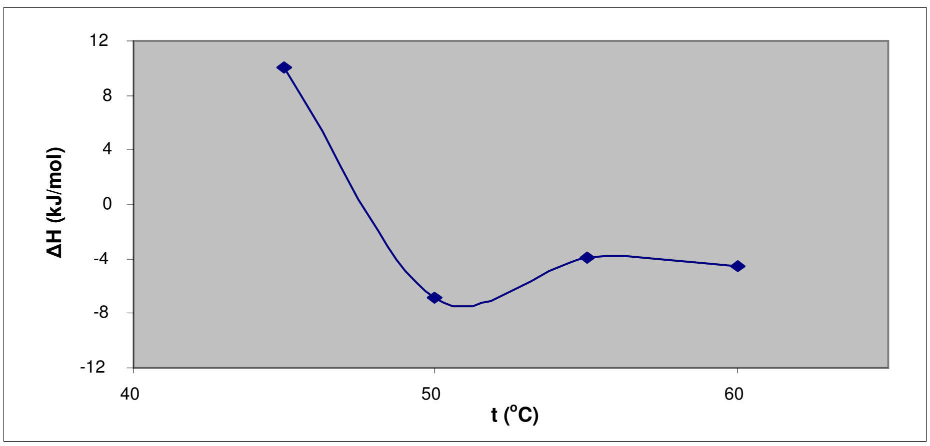

Figure D.5 : $\Delta H = f\,(t°C)$ Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

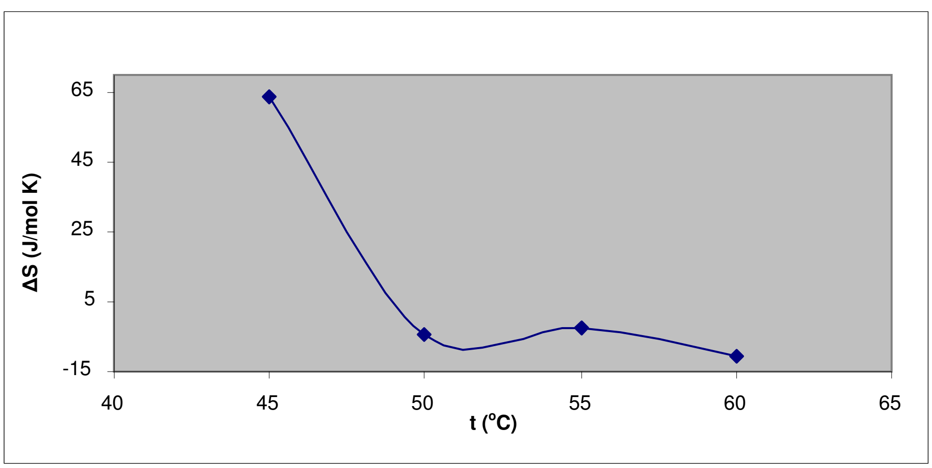

Figure D.6 : $\Delta S = f\,(t°C)$ Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) NaCl, (I=1 mol/L)

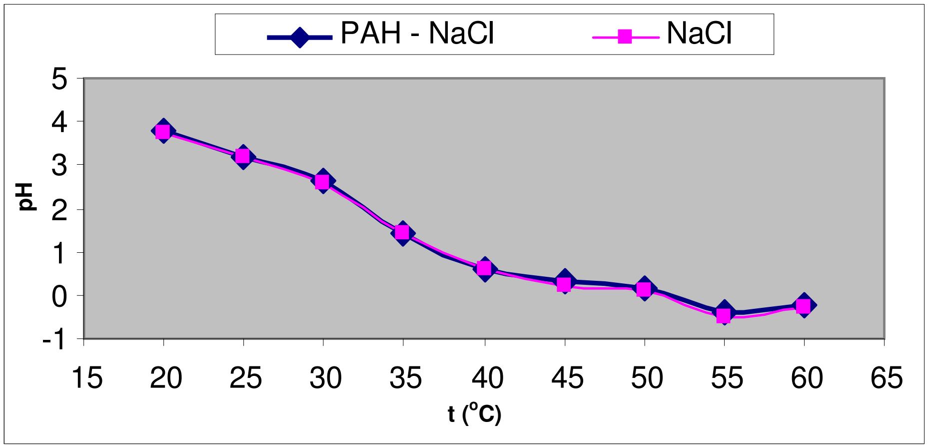

Figure D.7 : pH=f (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl ($I=1x10^{-1}$ mol/L)

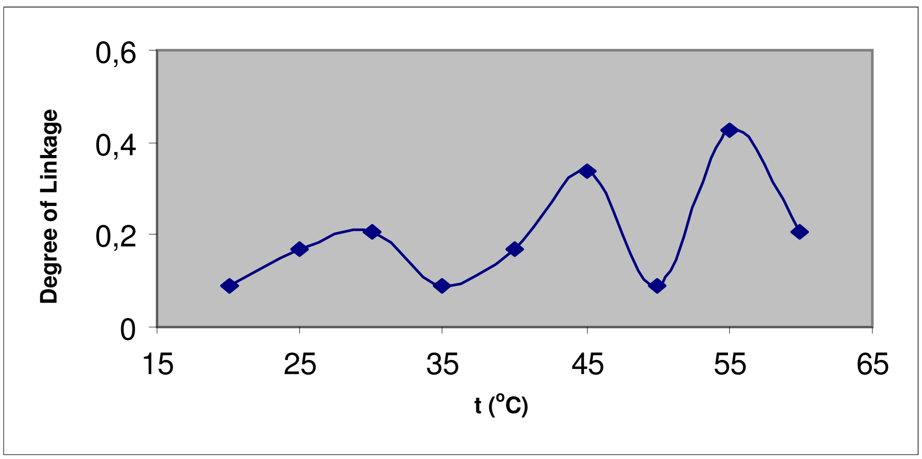

Figure D.8 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl ($I=1x10^{-1}$ mol/L)

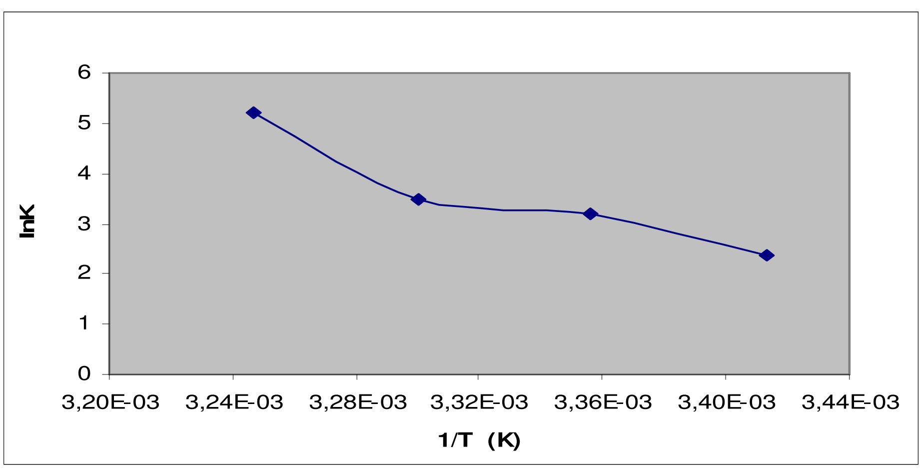

Figure D.9 : Curve of equilibrium constant $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl ($I=1x10^{-1}$ mol/L)

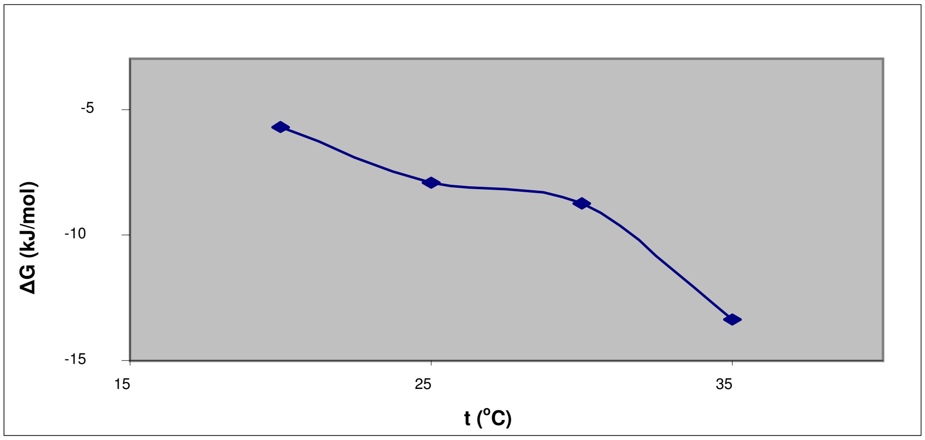

Figure D.10 :$\Delta G = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl (I=$1x10^{-1}$ mol/L)

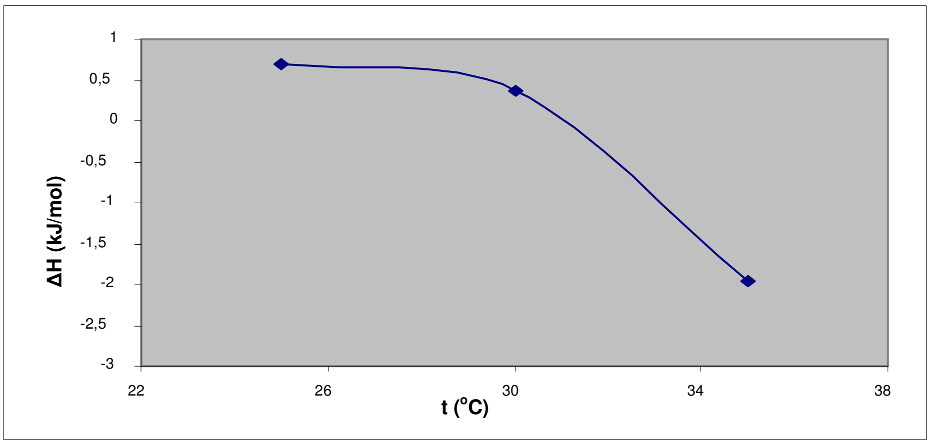

Figure D.11 :$\Delta H = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl (I=$1x10^{-1}$ mol/L)

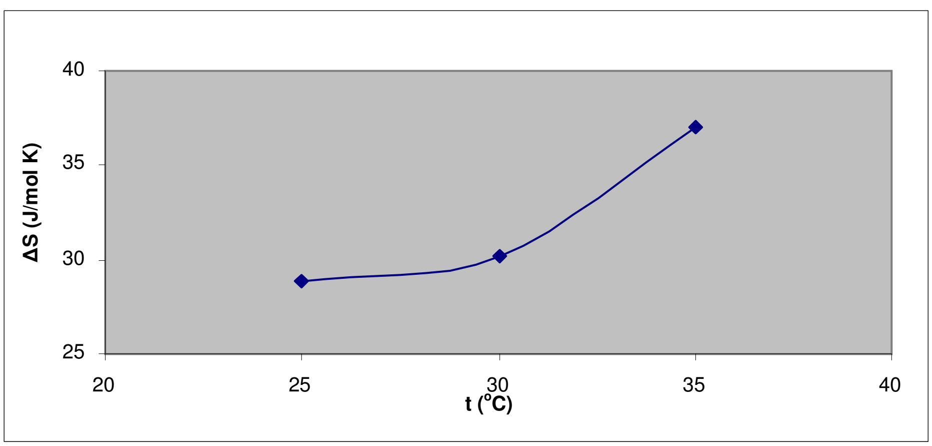

Figure D.12 :$\Delta S = f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) NaCl (I=$1x10^{-1}$ mol/L)

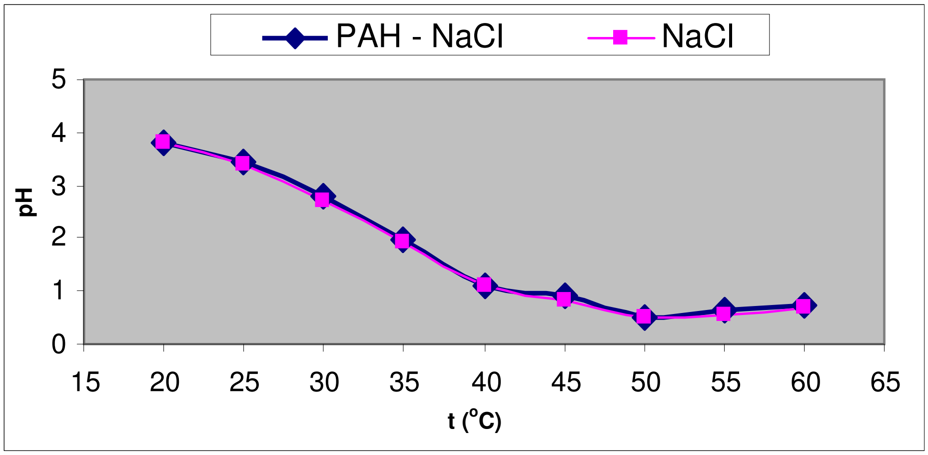

Figure D.13 : pH=f (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl, (I=$1x10^{-2}$ mol/L)

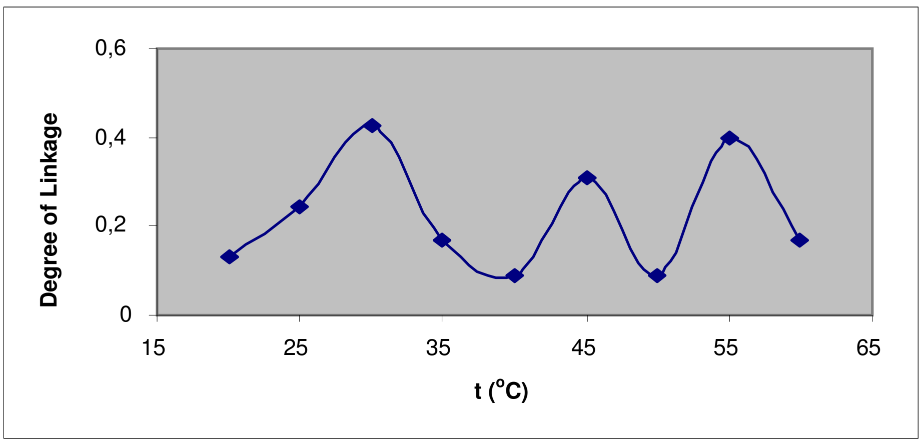

Figure D.14 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl , (I=$1x10^{-2}$ mol/L)

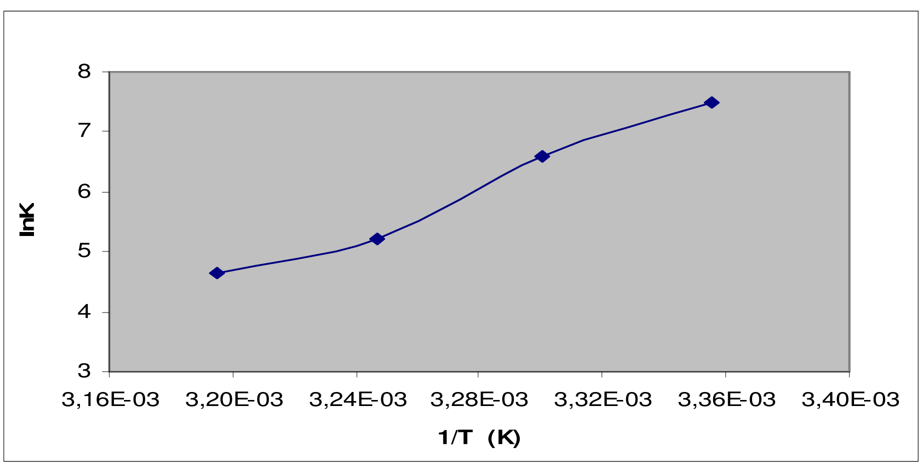

Figure D.15 : Curve of equilibrium constant $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl , (I=$1x10^{-2}$ mol/L)

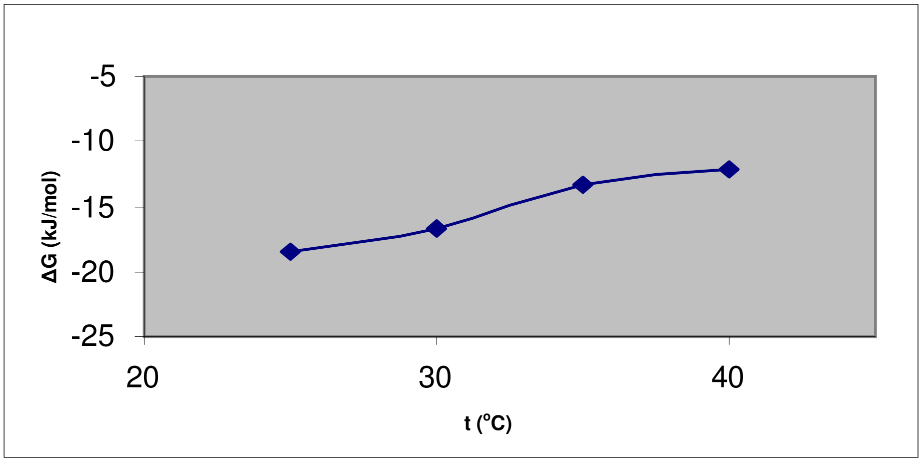

Figure D.16 :$\Delta G = f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl, ($I=1x10^{-2}$ mol/L)

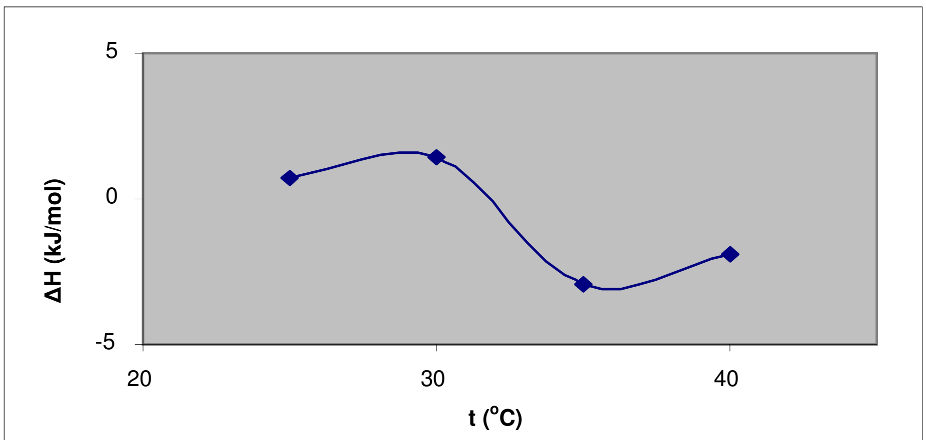

Figure D.17 :$\Delta H = f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl , ($I=1x10^{-2}$ mol/L)

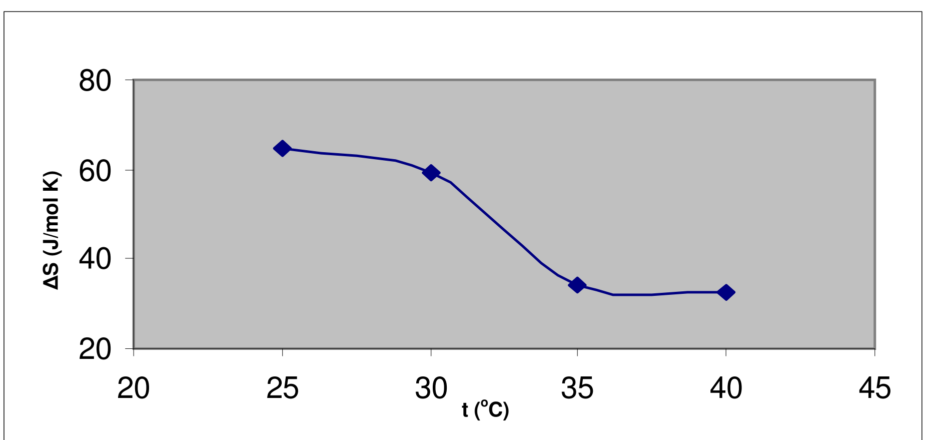

Figure D.18 :$\Delta S = f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) NaCl , ($I=1x10^{-2}$ mol/L)

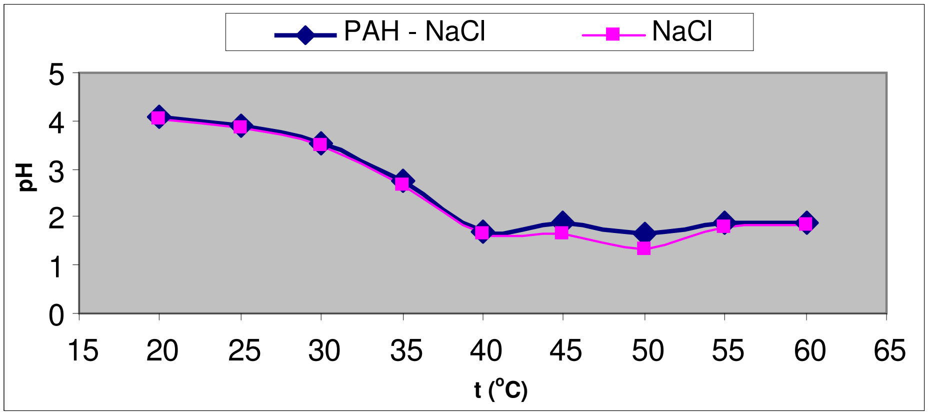

Figure D.19 :pH=f (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl, (I=$1x10^{-3}$ mol/L)

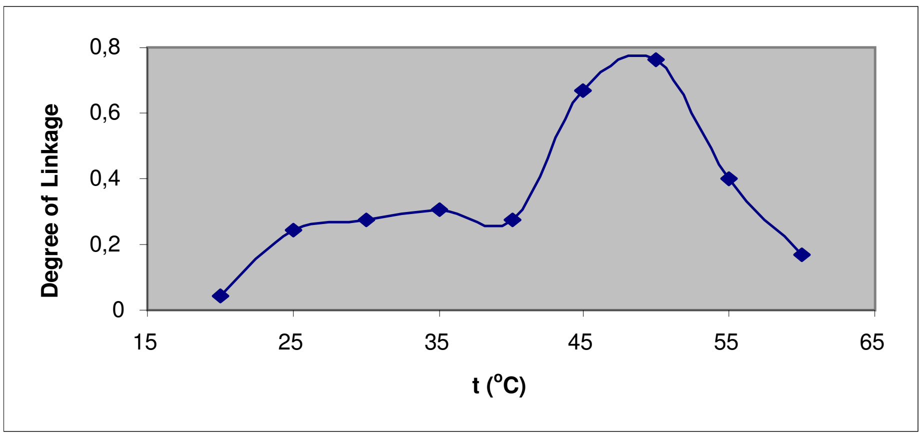

Figure D.20 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl , (I=$1x10^{-3}$ mol/L)

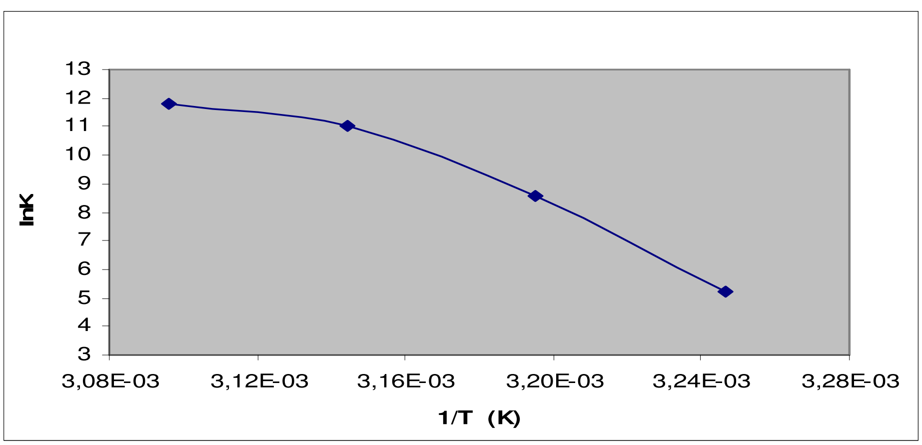

Figure D.21 : Curve of equilibrium constant $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl , (I=$1x10^{-3}$ mol/L)

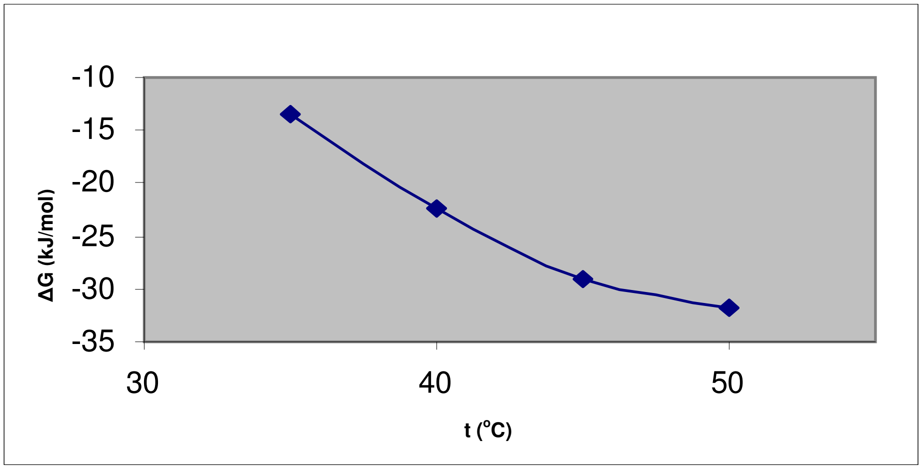

Figure D.22 :$\Delta G=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl , (I=$1x10^{-3}$ mol/L)

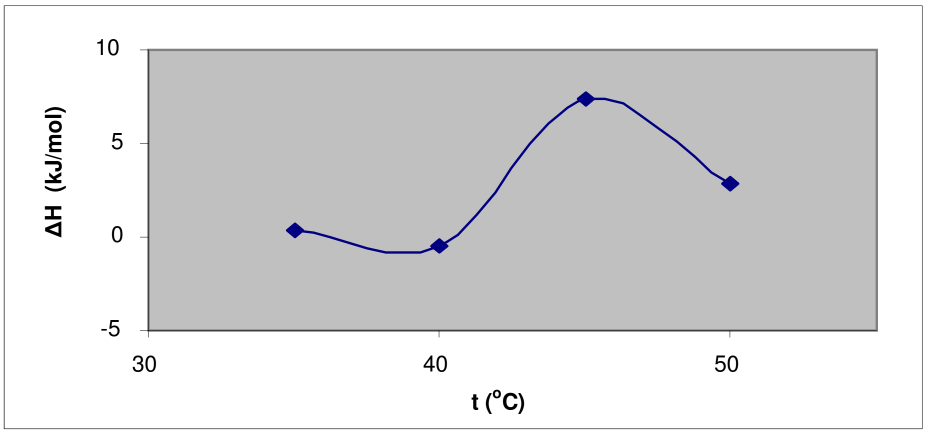

Figure D.23 :$\Delta H=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl , (I=$1x10^{-3}$ mol/L)

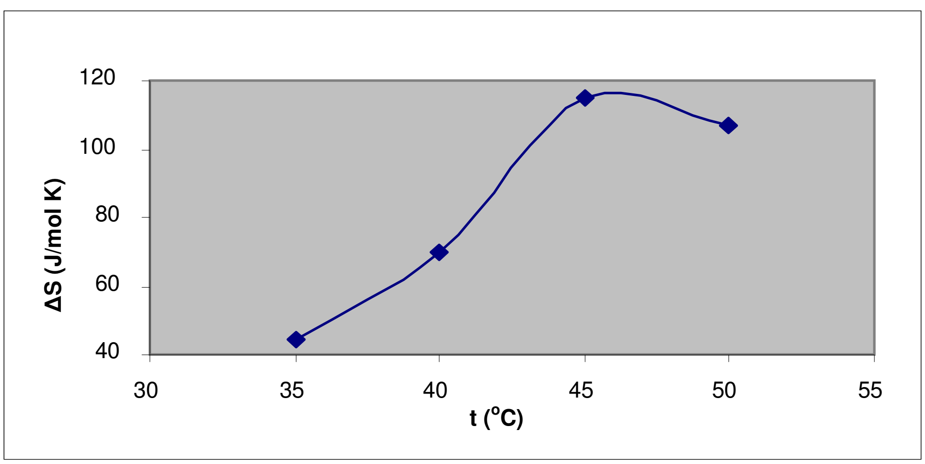

Figure D.24 :$\Delta S=f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) NaCl , (I=$1x10^{-3}$ mol/L)

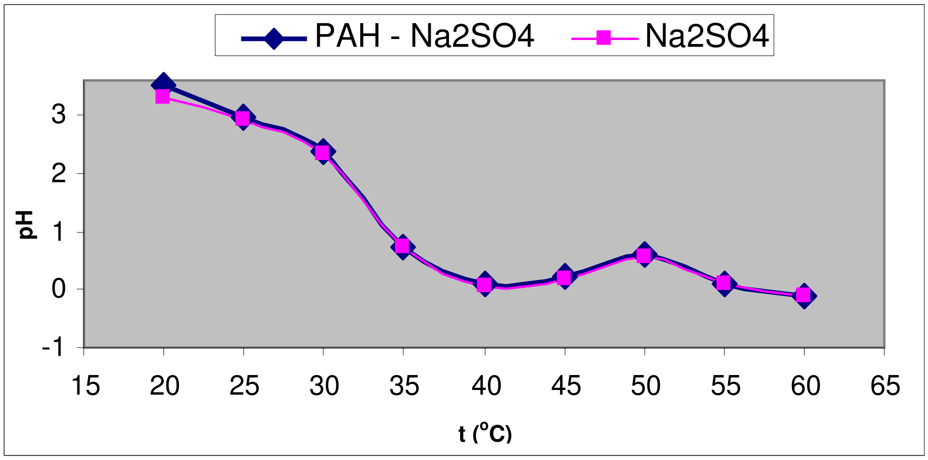

Figure D.25 : pH=*f* (t°C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

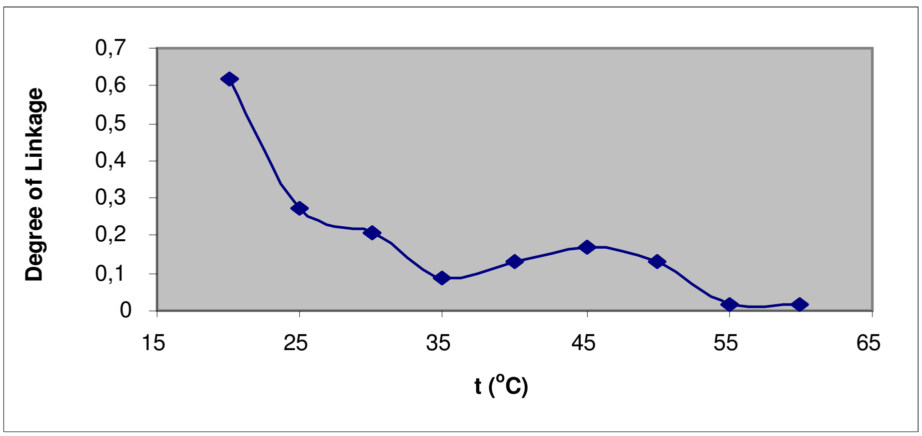

Figure D.26 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

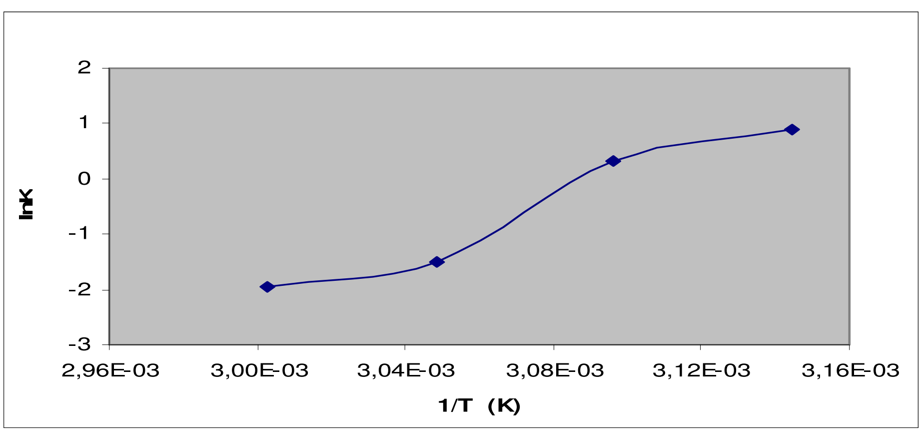

Figure D.27 : Curve of equilibrium constant $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

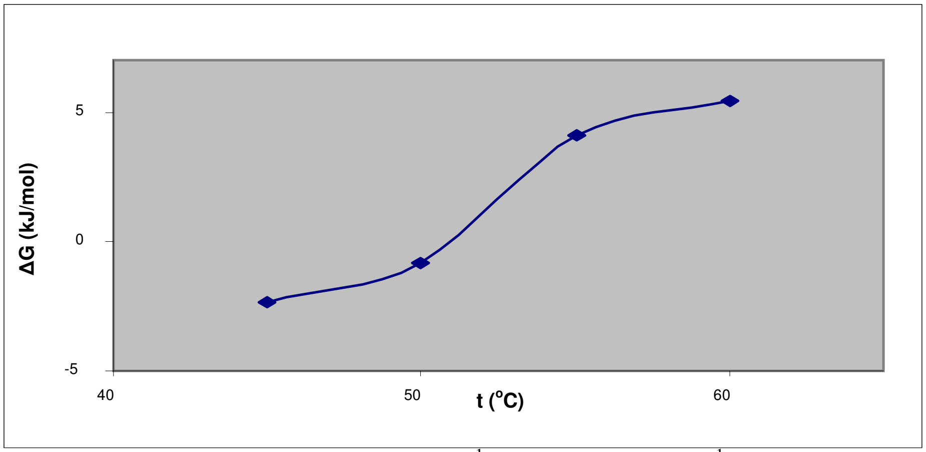

Figure D.28 :$\Delta G = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

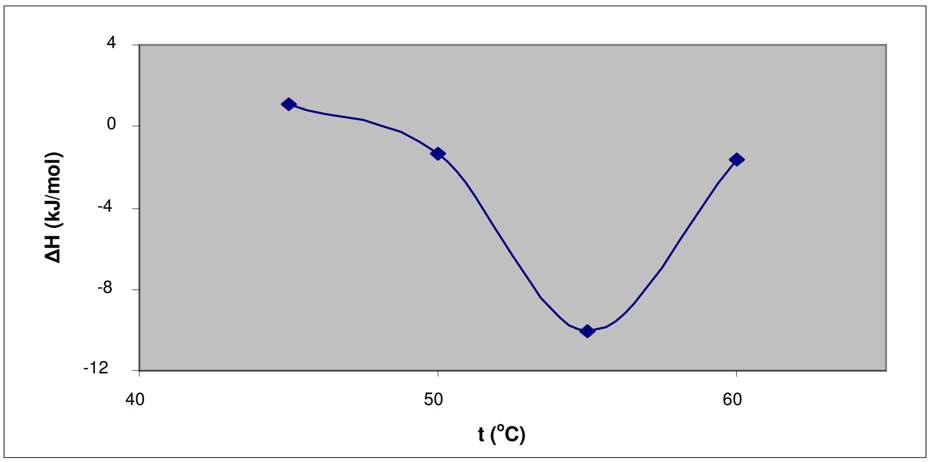

Figure D.29 :$\Delta H = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

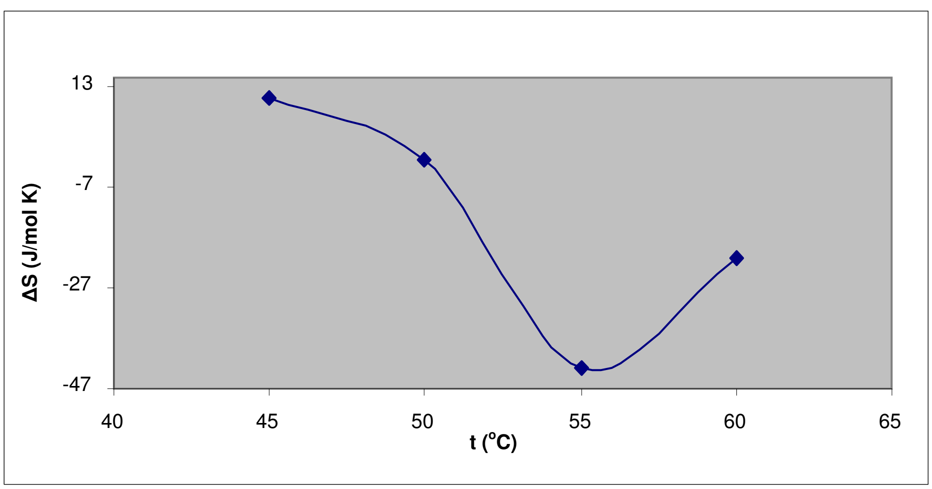

Figure D.30 :$\Delta S = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) Na_2SO_4 (I=1 mol/L)

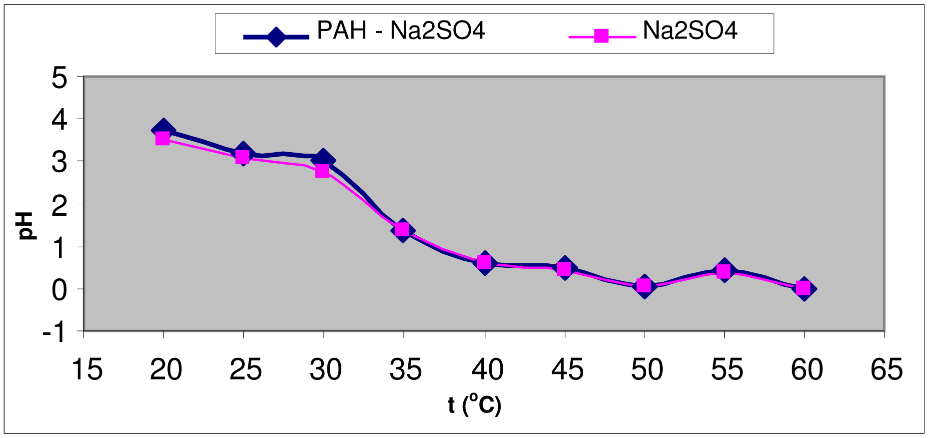

Figure D31 : pH=*f* (t°C) Curve of 1x10^{-2}(mol/L) PAH- 1x10^{-2}(mol/L) Na_2SO_4 (I=1x10^{-1} mol/L)

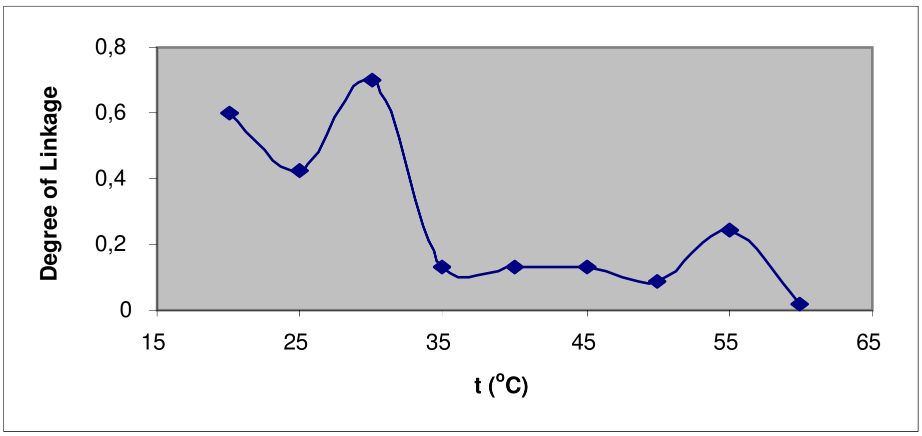

Figure D.32 : Degree of linkage, $\theta = f$ (t°C)Curve of 1x10^{-2}(mol/L) PAH- 1x10^{-2}(mol/L)Na_2SO_4 (I=1x10^{-1} mol/L)

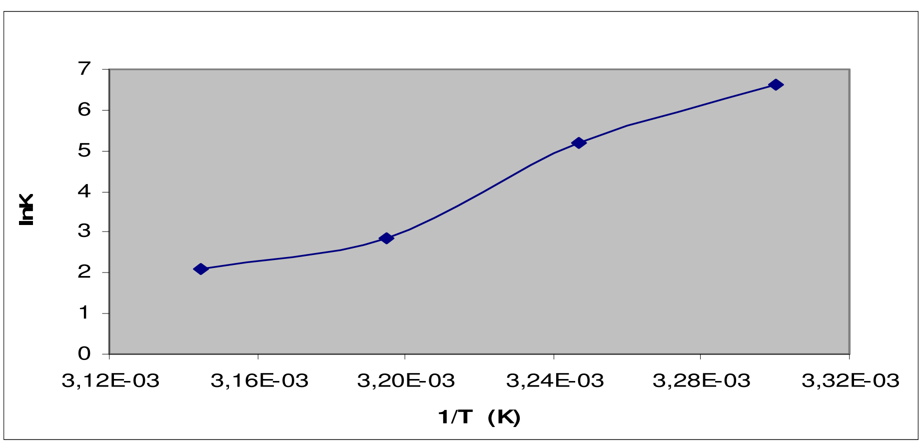

Figure D.33 : Curve of equilibrium constant 1x10^{-2}(mol/L) PAH- 1x10^{-2}(mol/L) Na_2SO_4 (I=1x10^{-1} mol/L)

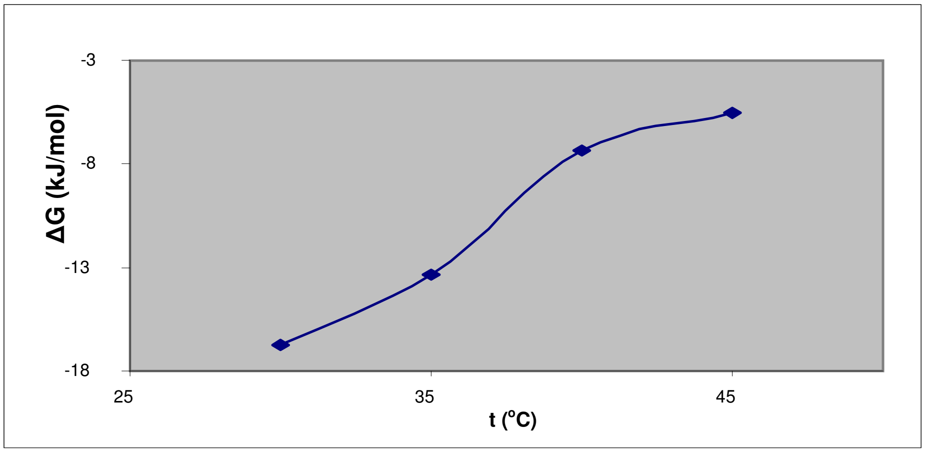

Figure D.34 :$\Delta G=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) Na_2SO_4 (I=$1x10^{-1}$ mol/L)

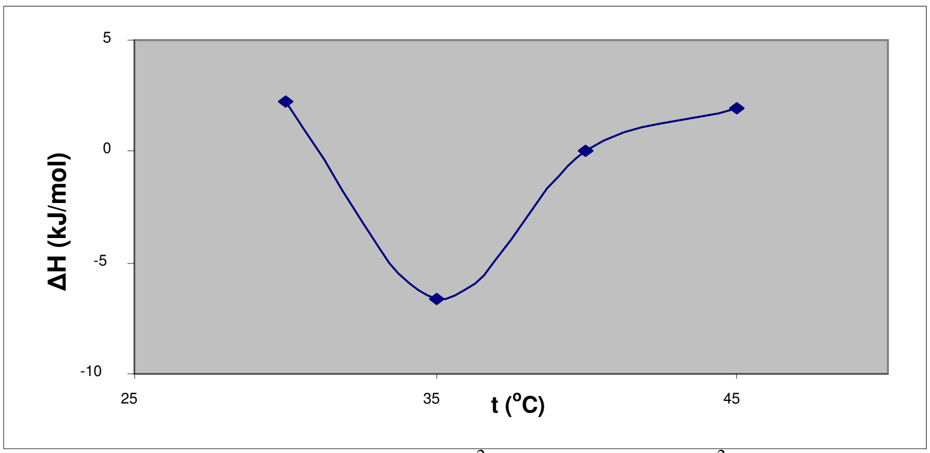

Figure D.35 :$\Delta H=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) Na_2SO_4 (I=$1x10^{-1}$ mol/L)

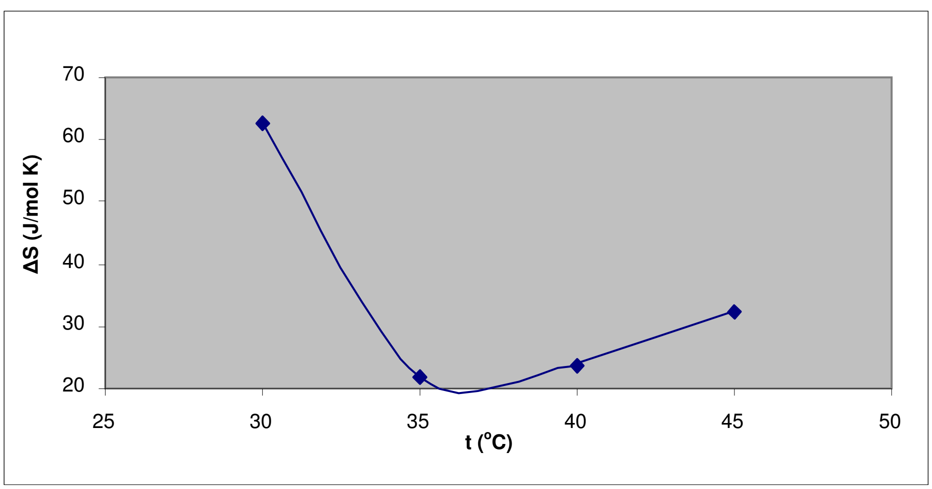

Figure D.36 :$\Delta S=f$ (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) Na_2SO_4 (I=$1x10^{-1}$ mol/L)

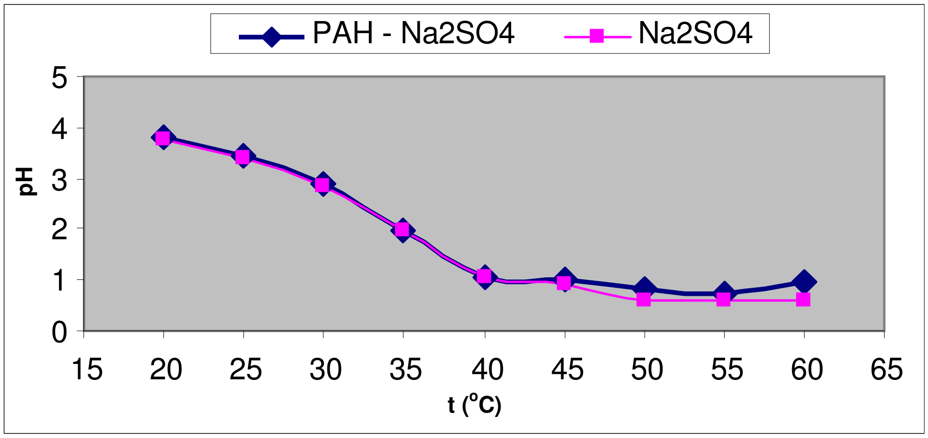

Figure D.37 :pH=f (t°C)Curve of 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) Na_2SO_4 , (I=1x10^{-2} mol/L)

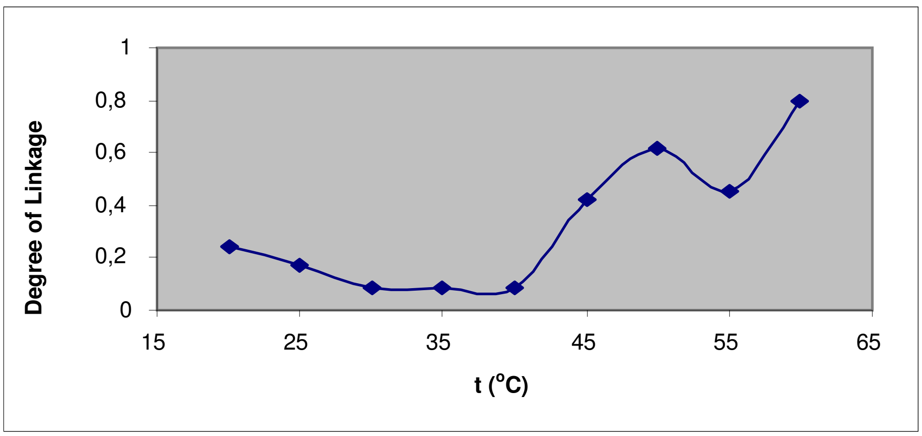

Figure D.38 : Degree of linkage,θ =f(t °C),Curve of 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L)Na_2SO_4, (I=1x10^{-2} mol/L)

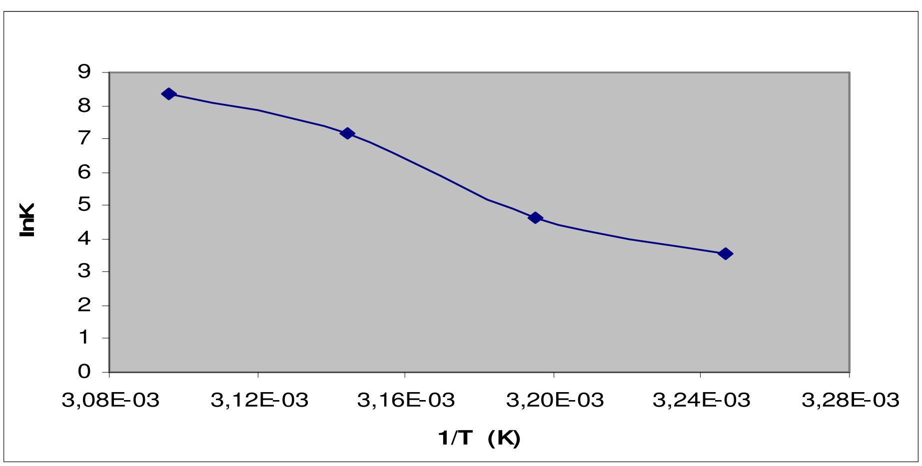

Figure D.39 : Curve of equilibrium constant 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) Na_2SO_4 (I=1x10^{-2} mol/L)

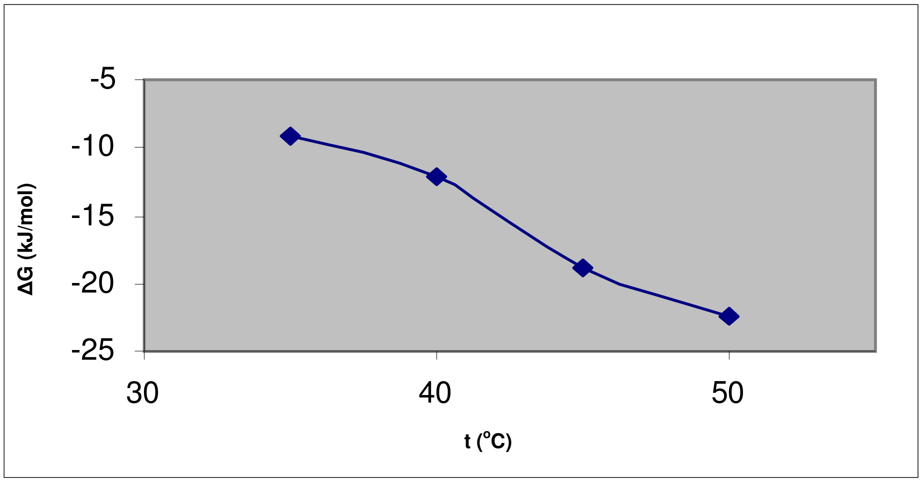

Figure D.40 : $\Delta G = f\ (t^{\circ}C)$ Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

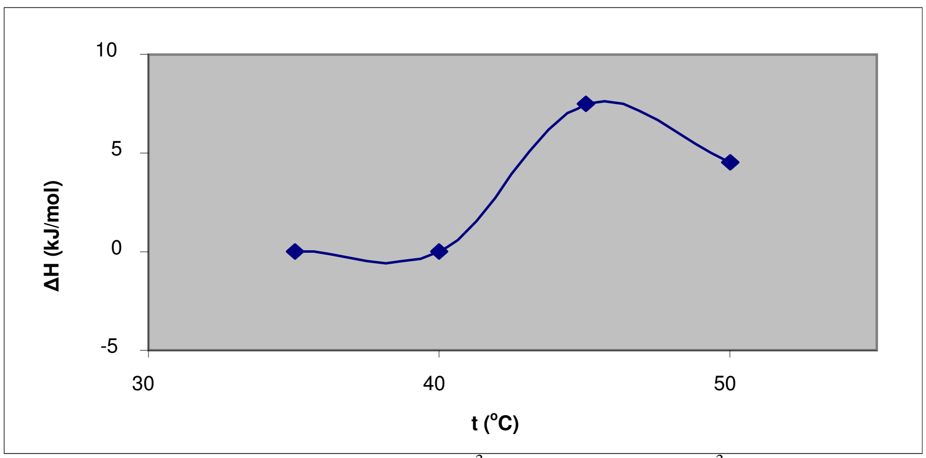

Figure D.41 : $\Delta H = f\ (t^{\circ}C)$ Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

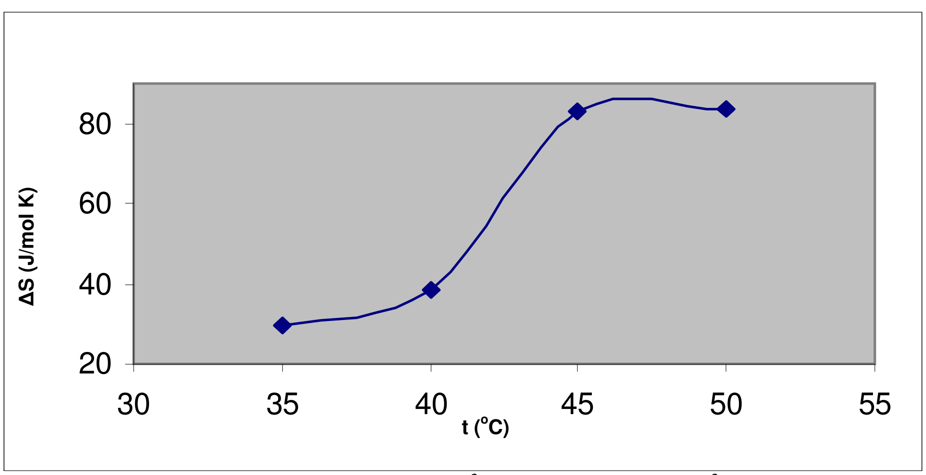

Figure D.42 : $\Delta S = f\ (t^{\circ}C)$ Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) Na_2SO_4, ($I=1x10^{-2}$ mol/L)

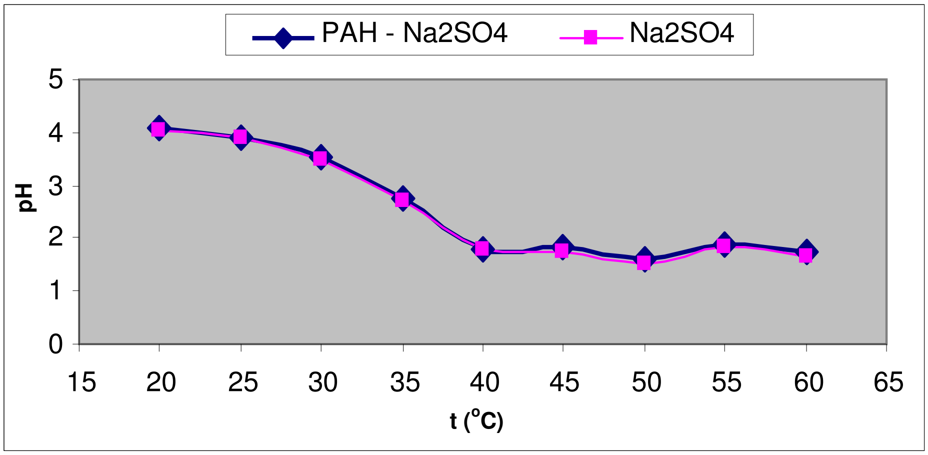

Figure D.43 :pH=*f* (t°C) Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L) Na_2SO_4 , (I=1x10^{-3} mol/L)

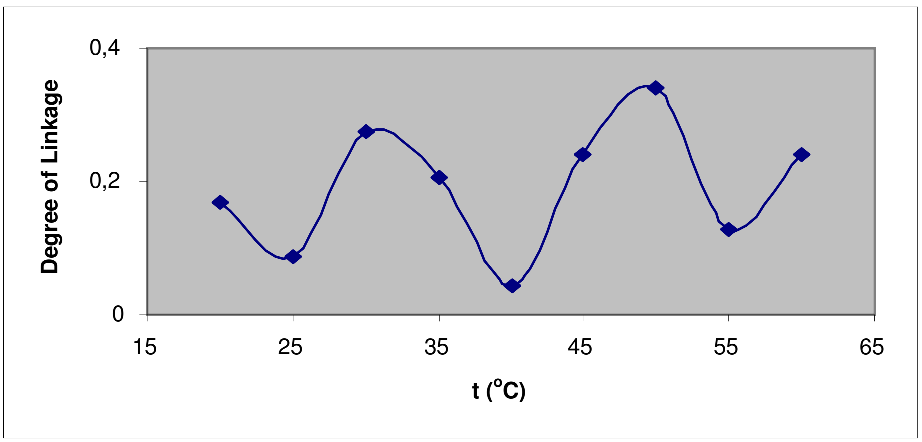

Figure D.44 : Degree of linkage, θ =*f* (t°C)Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L) Na_2SO_4 , (I=1x10^{-3} mol/L)

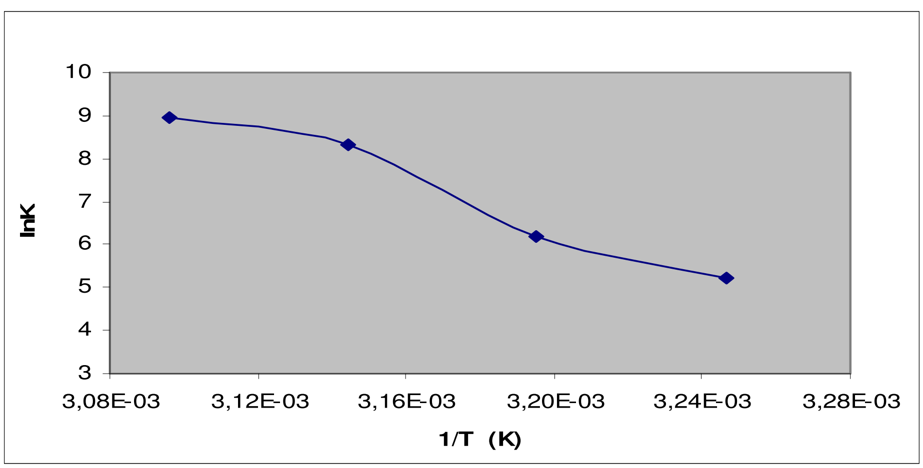

Figure D.45 : Curve of equilibrium constant 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L) Na_2SO_4, (I=1x10^{-3} mol/L)

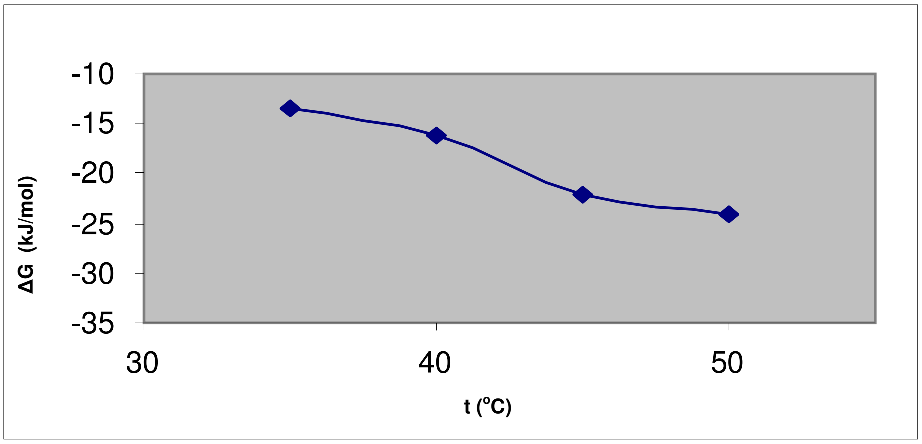

Figure D.46 :$\Delta G = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) Na_2SO_4, (I=$1x10^{-3}$ mol/L)

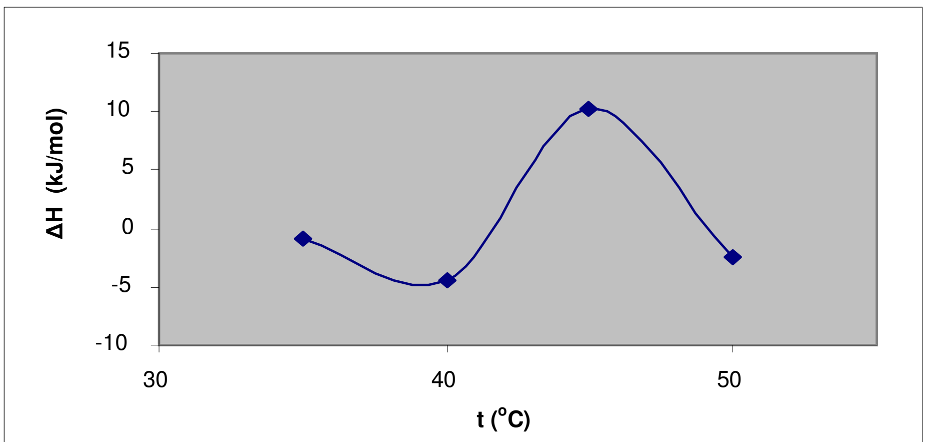

Figure D.47 :$\Delta H = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) Na_2SO_4, (I=$1x10^{-3}$ mol/L)

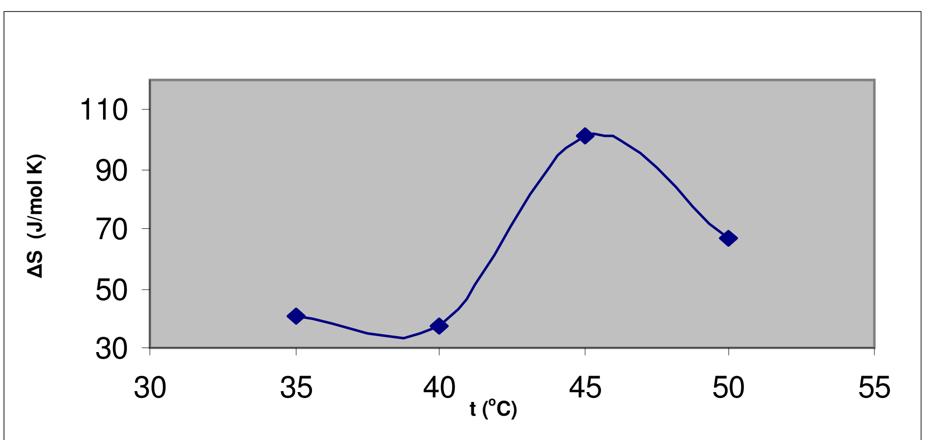

Figure D.48 :$\Delta S = f$ (t˚C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)Na_2SO_4, (I=$1x10^{-3}$ mol/L)

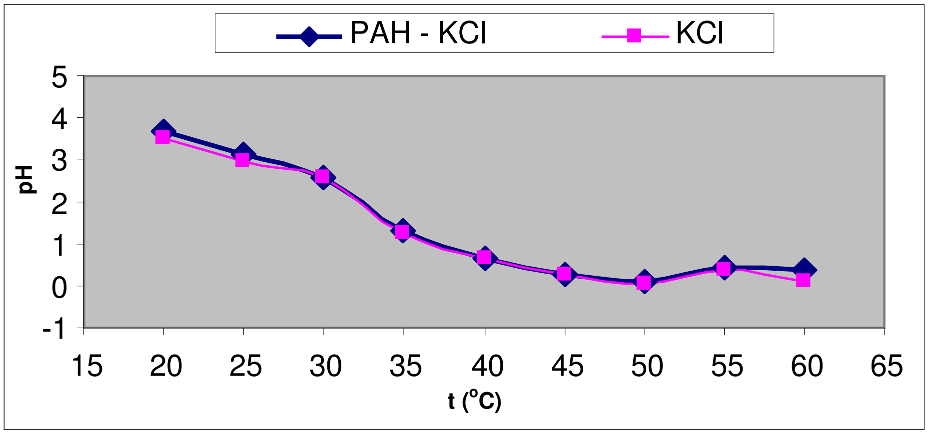

Figure D.49 : pH=*f* (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L)KCl, (I=$1x10^{-1}$ mol/L)

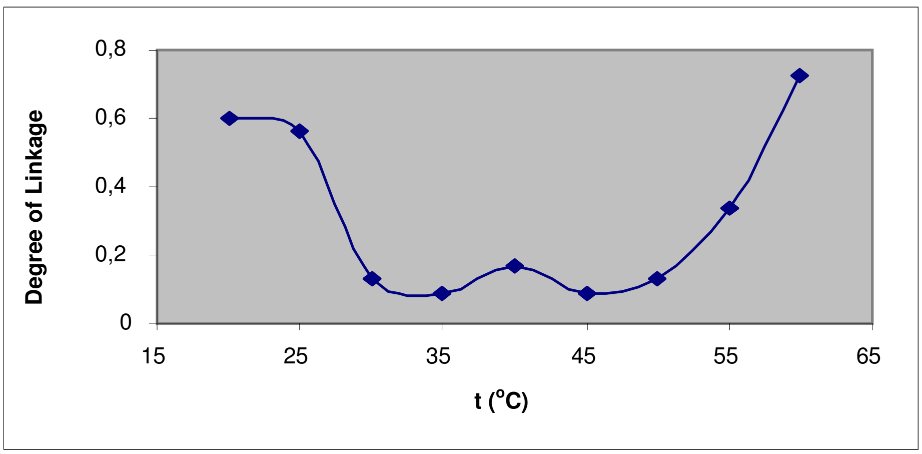

Figure D.50 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L)KCl, (I=$1x10^{-1}$ mol/L)

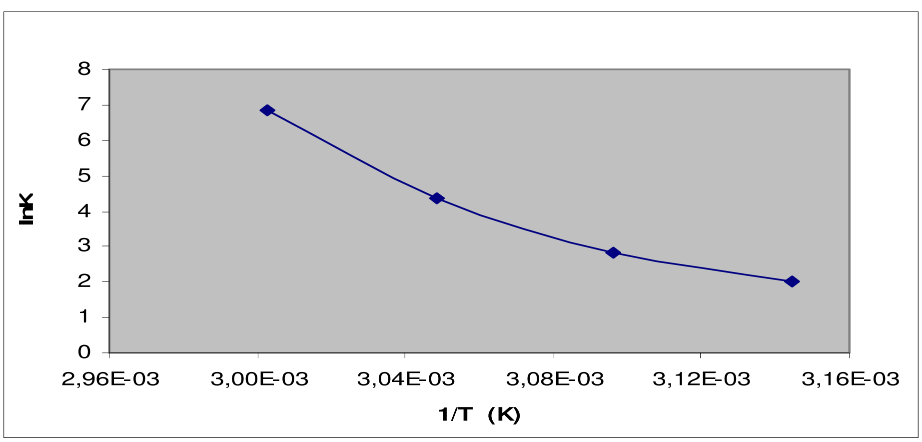

Figure D.51 : Curve of equilibrium constant $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

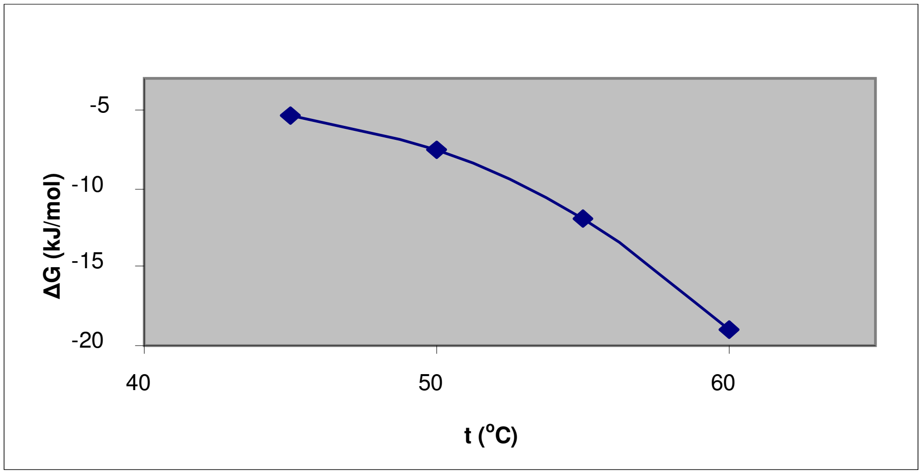

Figure D.52 : $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

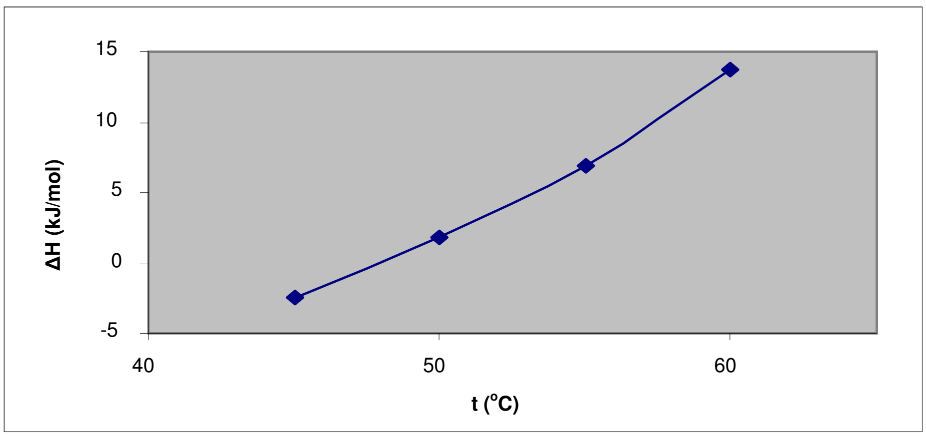

Figure D.53 : $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

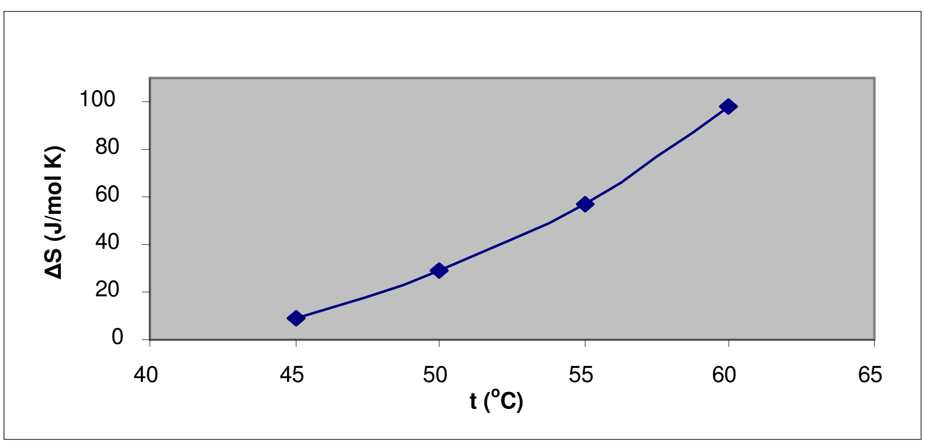

Figure D.54 : $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) KCl, (I=$1x10^{-1}$ mol/L)

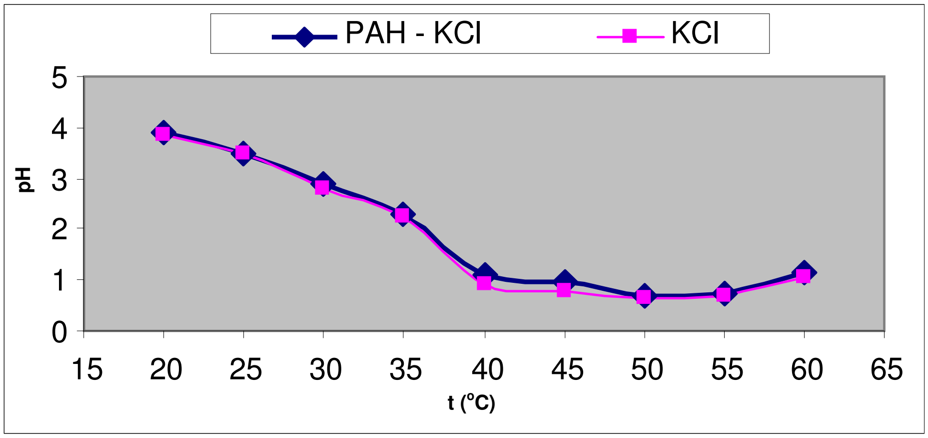

Figure D.55 : pH=f (t°C) Curve of $1x10^{-3}$(mol/L)PAH- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

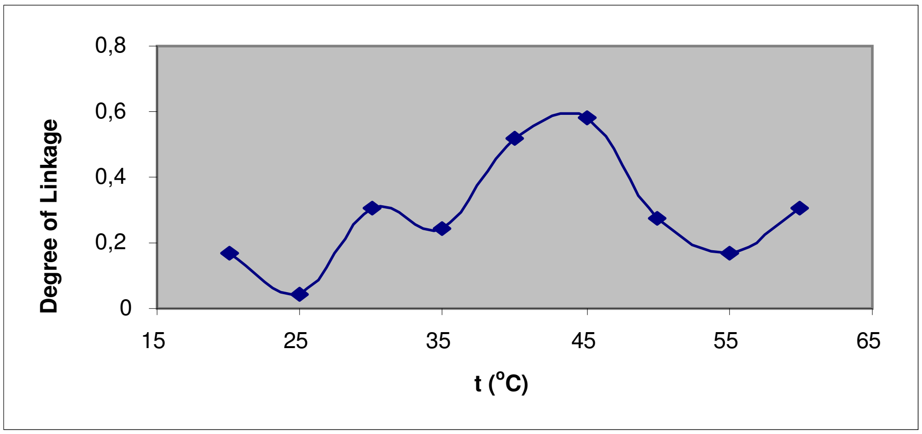

Figure D.56 : Degree of linkage, $\theta = f$ (t°C)Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) KCl, (I=$1x10^{-2}$ mol/L)

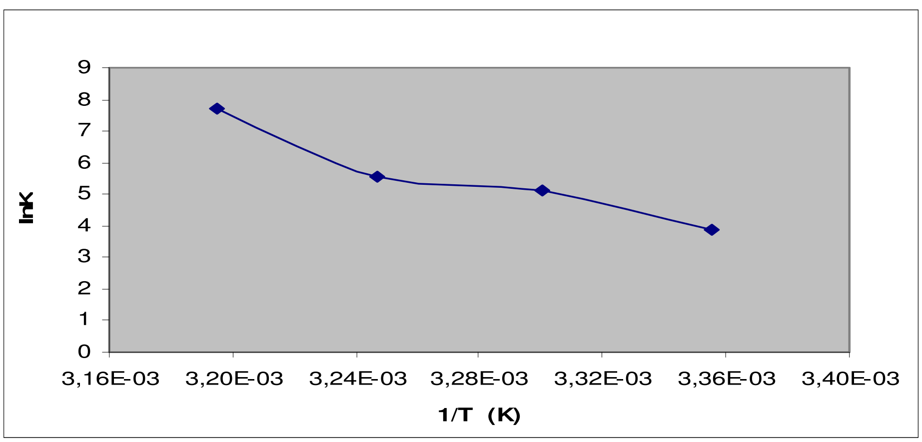

Figure D.57 : Curve of equilibrium constant $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) KCl (I=$1x10^{-2}$ mol/L)

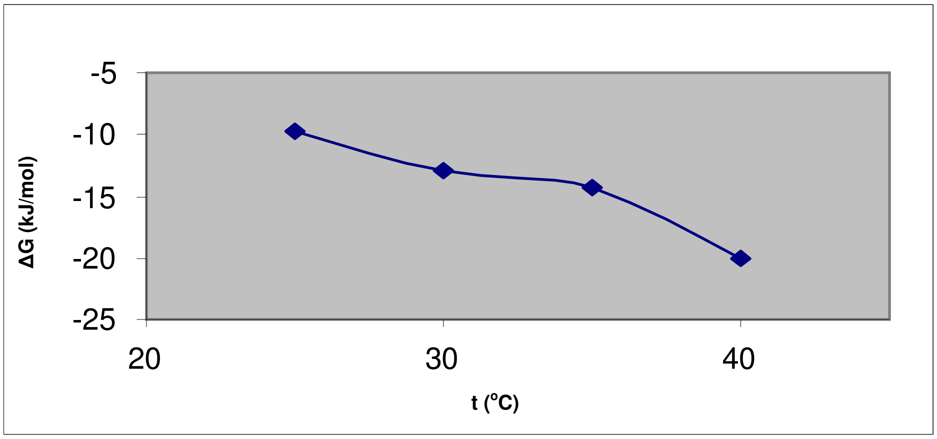

Figure D.58 :$\Delta G = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) KCl , (I=$1x10^{-2}$ mol/L)

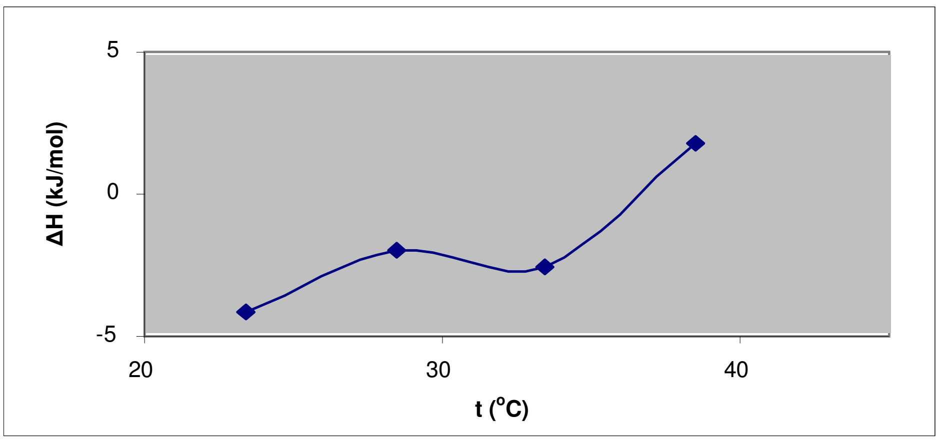

Figure D.59 :$\Delta H = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) KCl , (I=$1x10^{-2}$ mol/L)

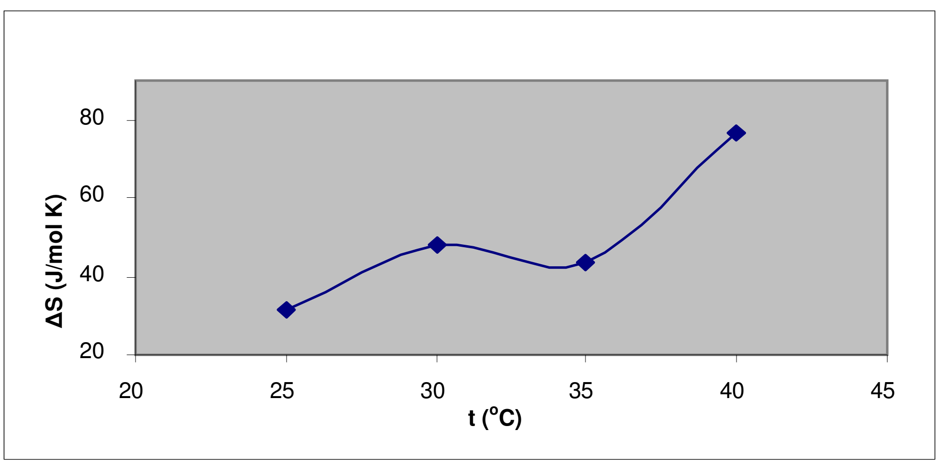

Figure D.60 :$\Delta S = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) KCl , (I=$1x10^{-2}$ mol/L)

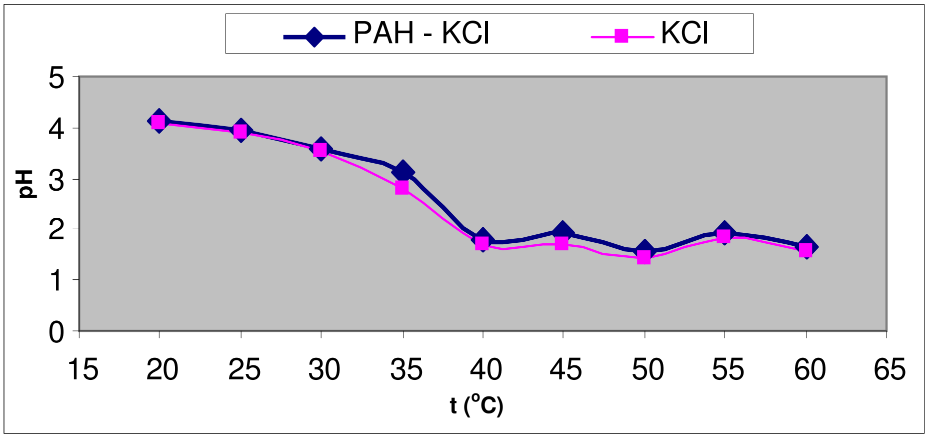

Figure D.61 : pH=f (t°C) Curve of 1x101x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)KCl (I=1x10^{-3} mol/L)

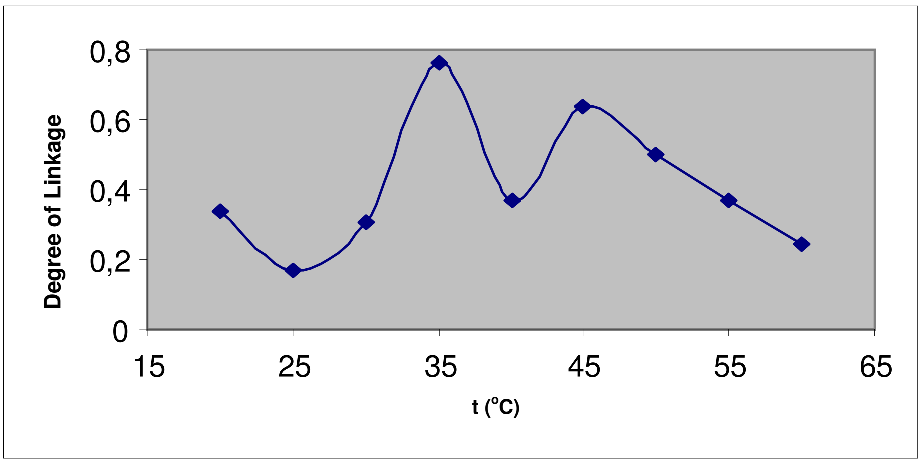

Figure D.62 : Degree of linkage, θ =f (t°C) Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)KCl , (I=1x10^{-3} mol/L)

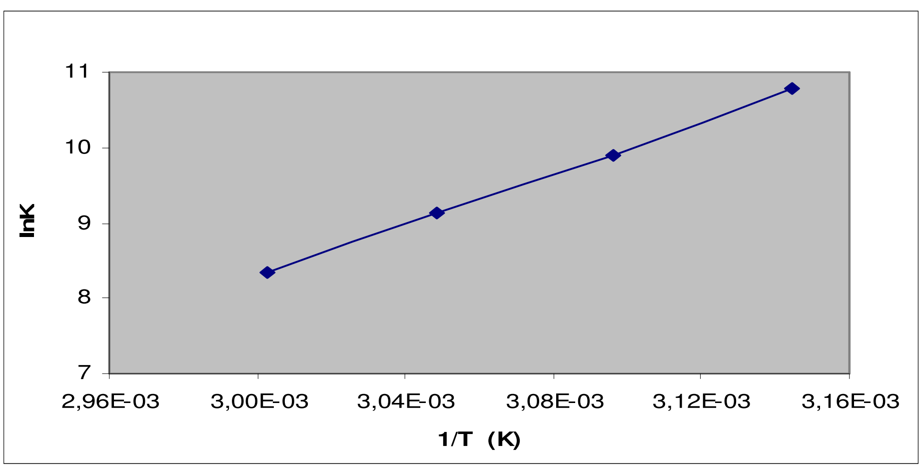

Figure D.63 : Curve of equilibrium constant 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)KCl, (I=1x10^{-3} mol/L)

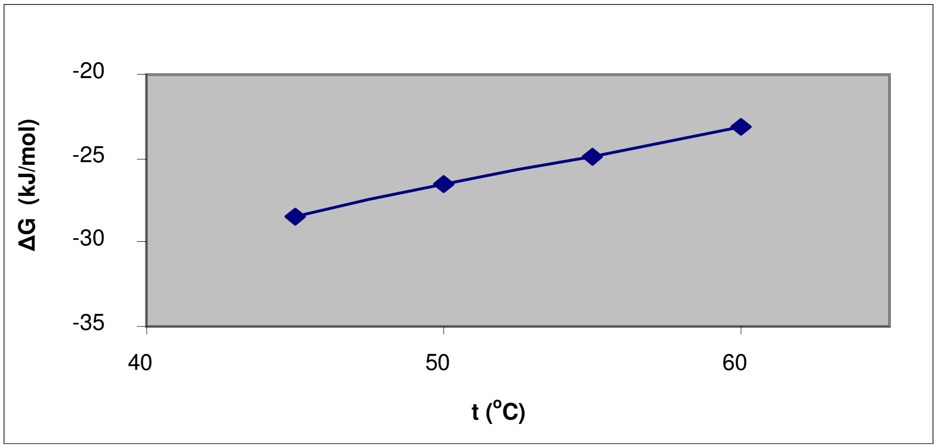

Figure D.64 :$\Delta G = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)KCl , ($I=1x10^{-3}$ mol/L)

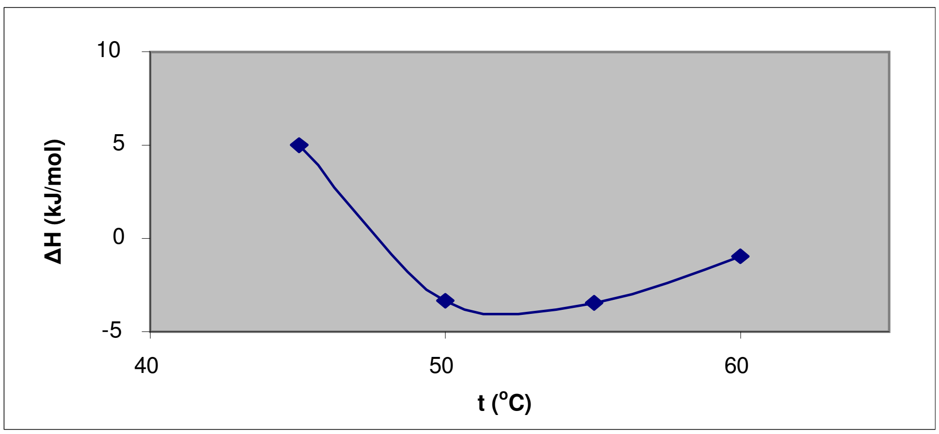

Figure D.65 :$\Delta H = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)KCl, ($I=1x10^{-3}$ mol/L)

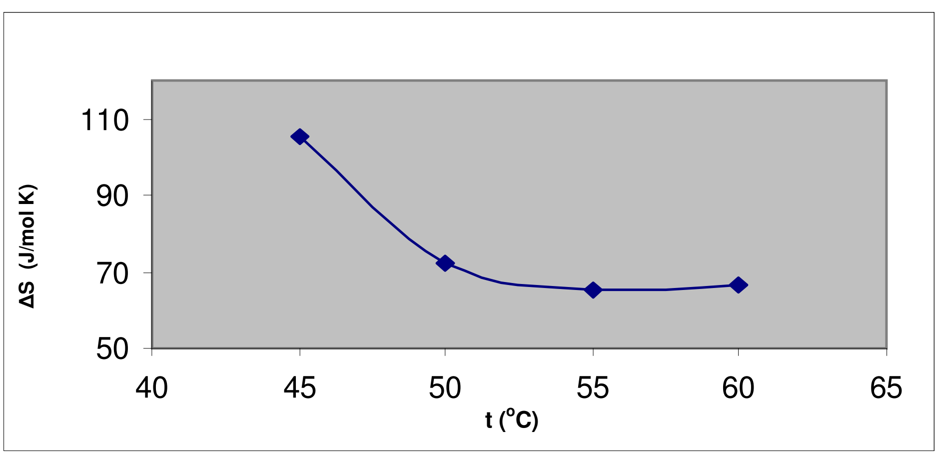

Figure D.66 :$\Delta S = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)KCl , ($I=1x10^{-3}$ mol/L)

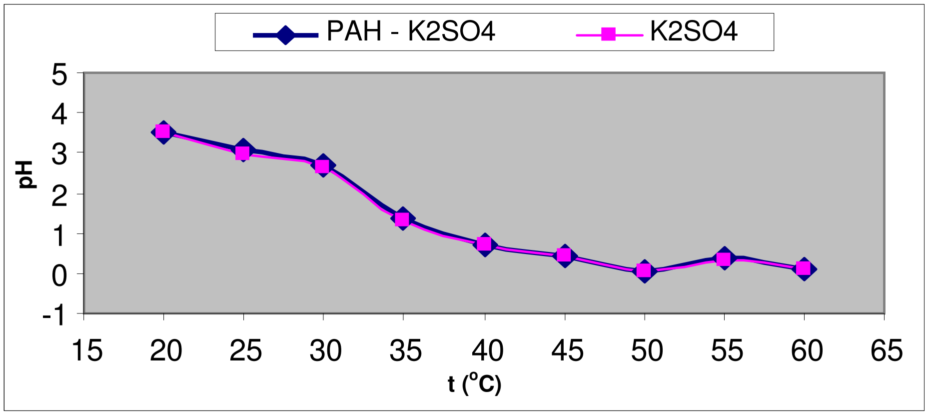

Figure D.67 :pH=*f* (t°C) Curve of $1x10^{-2}$(mol/L)PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

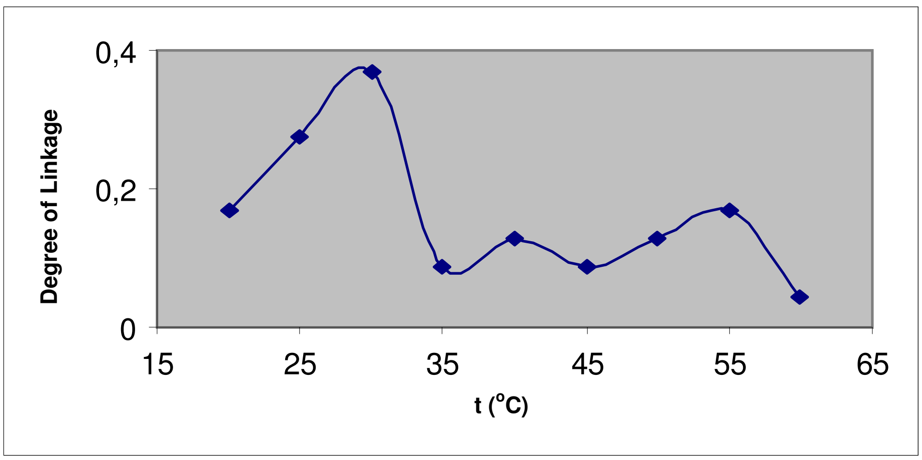

Figure D.68 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

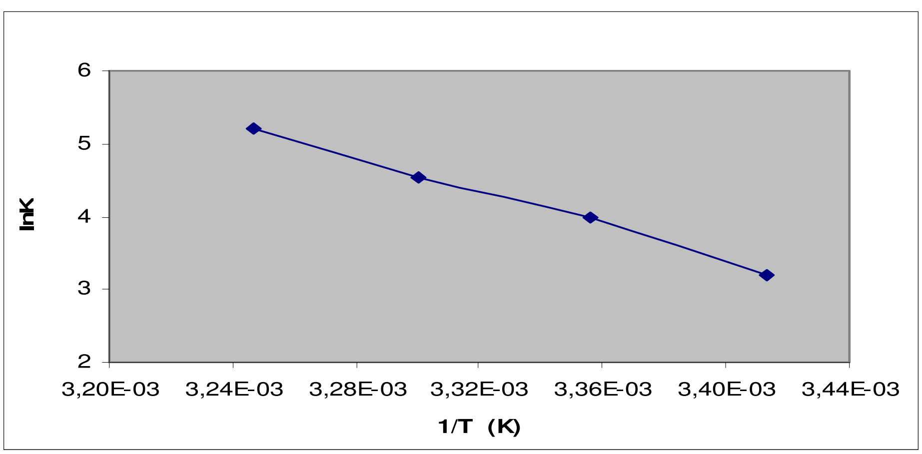

Figure D.69 : Curve of equilibrium constant $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I=1x10^{-1}$ mol/L)

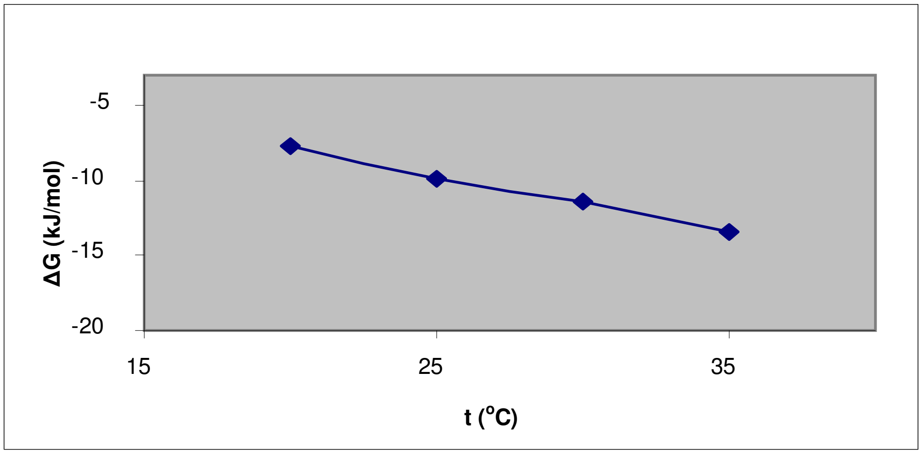

Figure D.70 :$\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I = 1x10^{-1}$ mol/L)

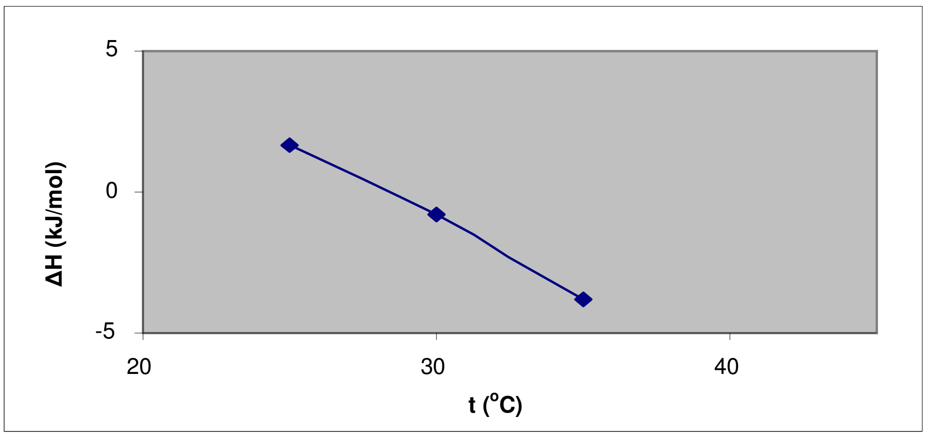

Figure D.71 :$\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I = 1x10^{-1}$ mol/L)

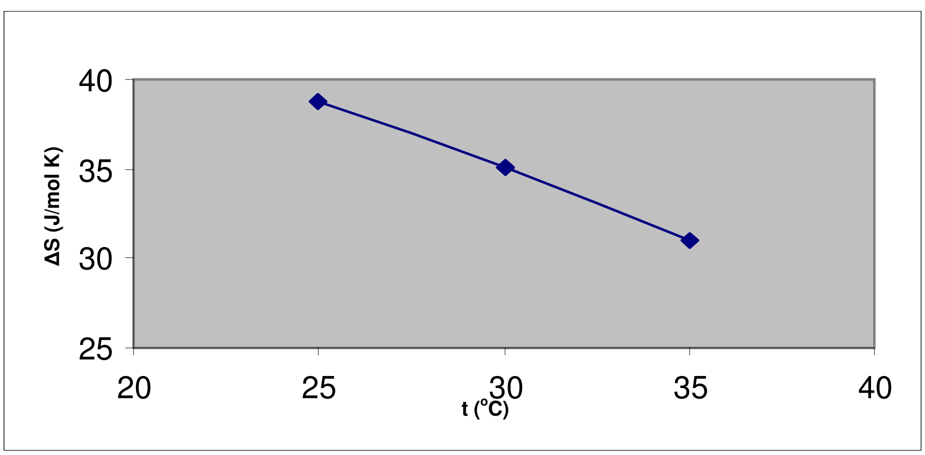

Figure D.72 :$\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) K_2SO_4, ($I = 1x10^{-1}$ mol/L)

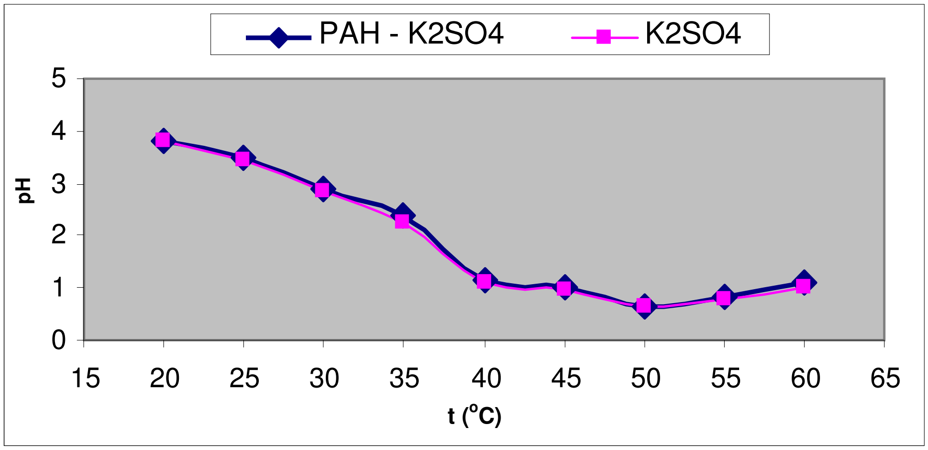

Figure D.73 :pH=f (t˚C) Curve of 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) K_2SO_4, (I=1x10^{-2} mol/L)

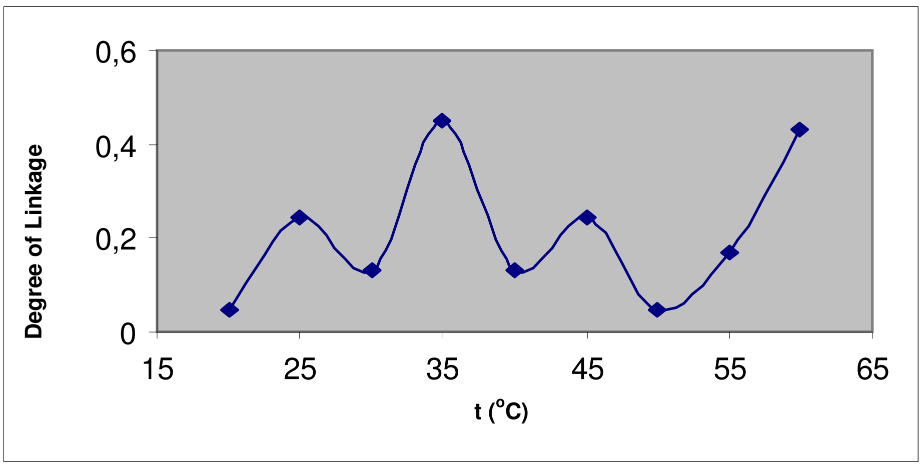

Figure D.74 : Degree of linkage, θ =f (t˚C) Curve of 1x10^{-3}(mol/L) PAH-1x10^{-3}(mol/L) K_2SO_4, (I=1x10^{-2} mol/L)

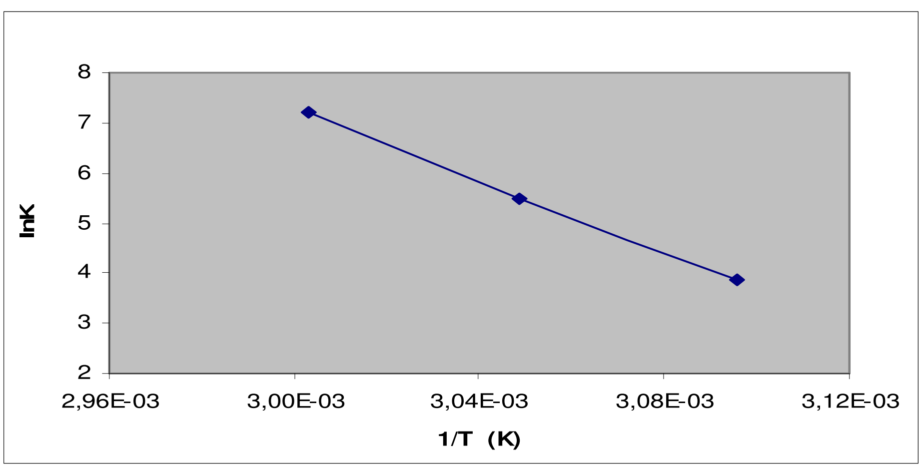

Figure D.75 : Curve of equilibrium constant 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) K_2SO_4, (I=1x10^{-2} mol/L)

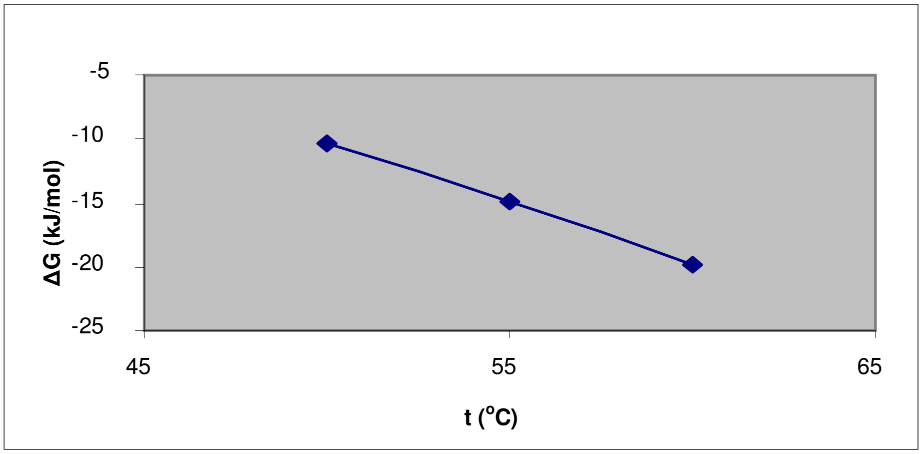

Figure D.76 :$\Delta G=f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) K_2SO_4, ($I=1x10^{-2}$ mol/L)

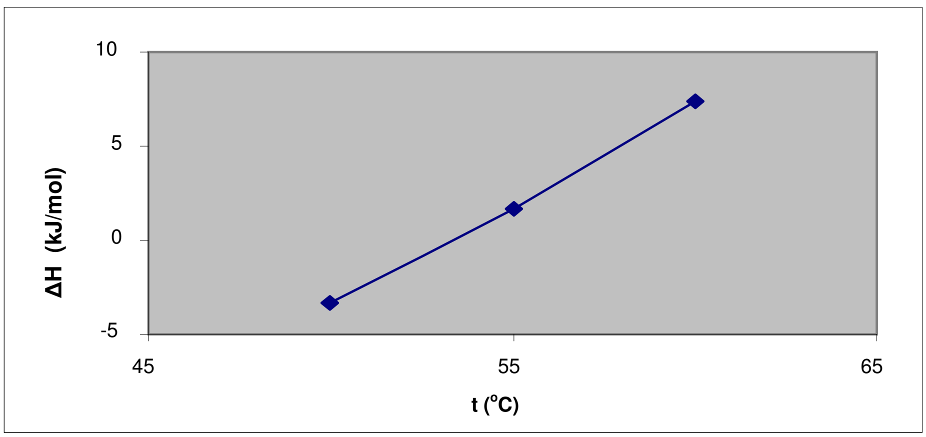

Figure D.77 :$\Delta H=f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) K_2SO_4, ($I=1x10^{-2}$ mol/L)

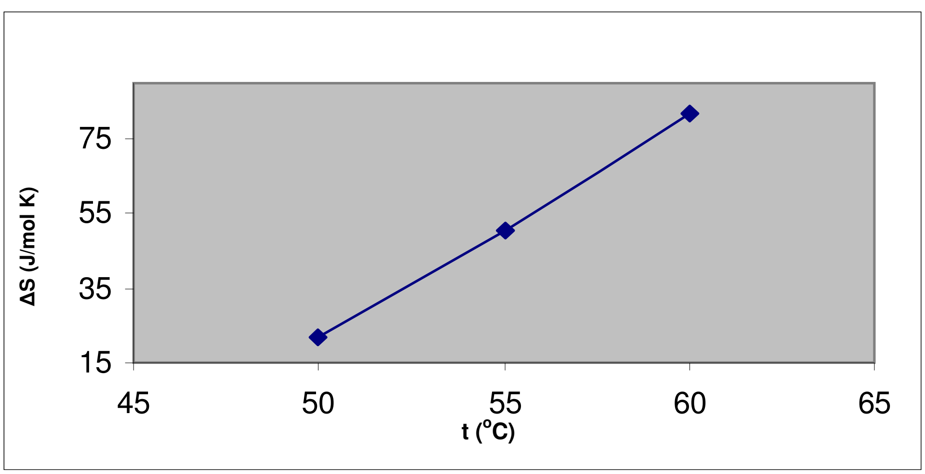

Figure D.78 :$\Delta S=f$ (t˚C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) K_2SO_4, ($I=1x10^{-2}$ mol/L)

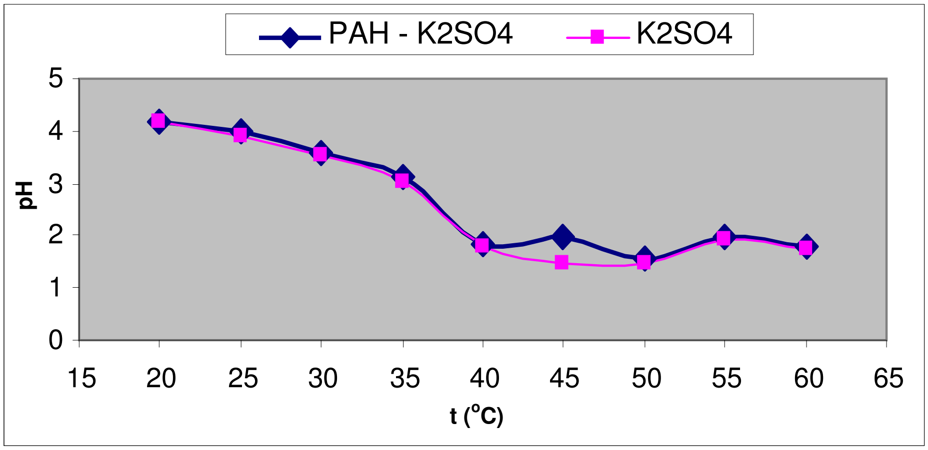

Figure D.79 :pH=*f* (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)K_2SO_4, ($I=1x10^{-3}$ mol/L)

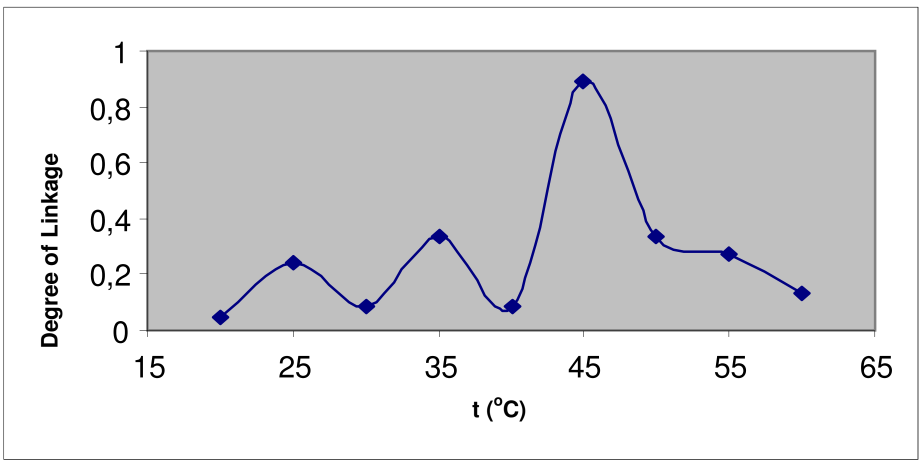

Figure D.80 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)K_2SO_4, ($I=1x10^{-3}$ mol/L)

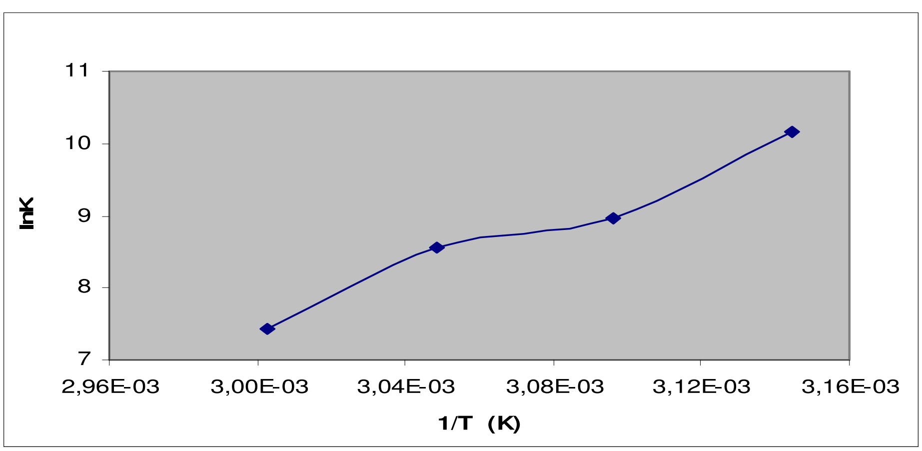

Figure D.81 : Curve of equilibrium constant $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L)K_2SO_4, ($I=1x10^{-3}$ mol/L)

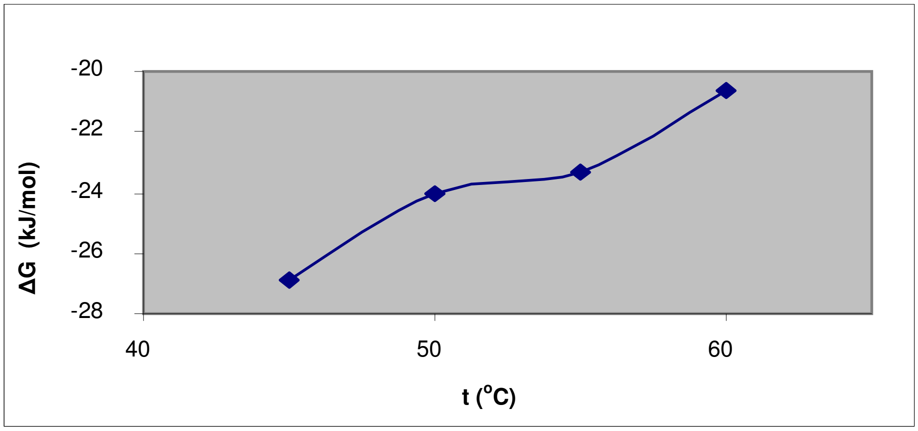

Figure D.82 :ΔG=ƒ (t˚C) Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)K_2SO_4, (I=1x10^{-3} mol/L)

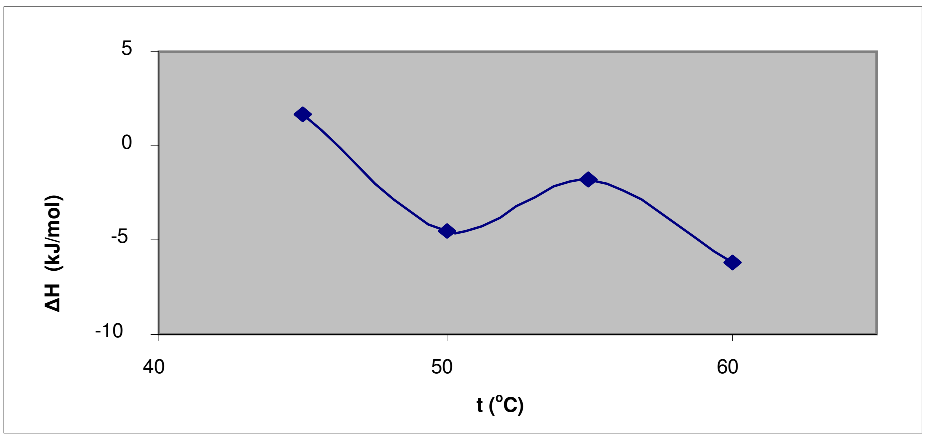

Figure D.83 :ΔH=ƒ (t˚C) Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)K_2SO_4, (I=1x10^{-3} mol/L)

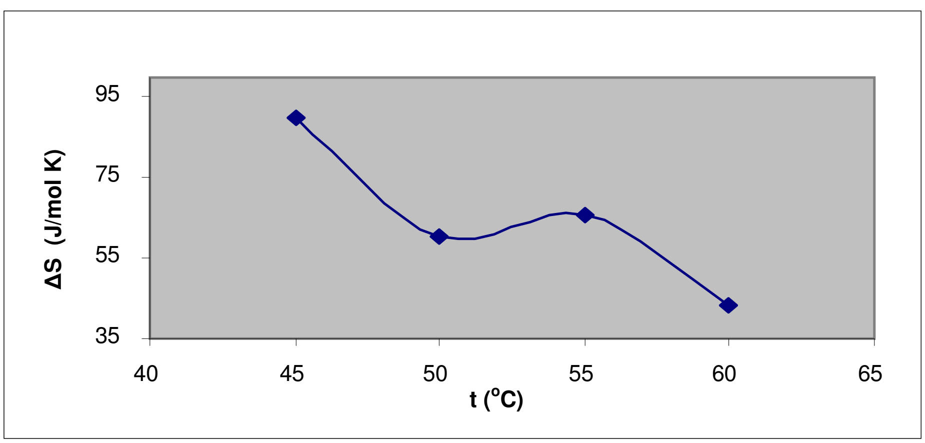

Figure D.84 :ΔS=ƒ (t˚C) Curve of 1x10^{-4}(mol/L) PAH- 1x10^{-4}(mol/L)K_2SO_4, (I=1x10^{-3} mol/L)

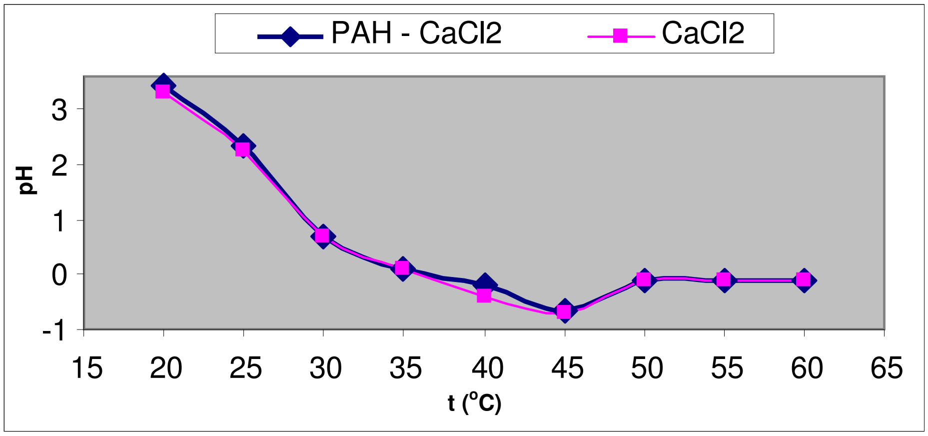

Figure D.85 : pH=f (t°C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

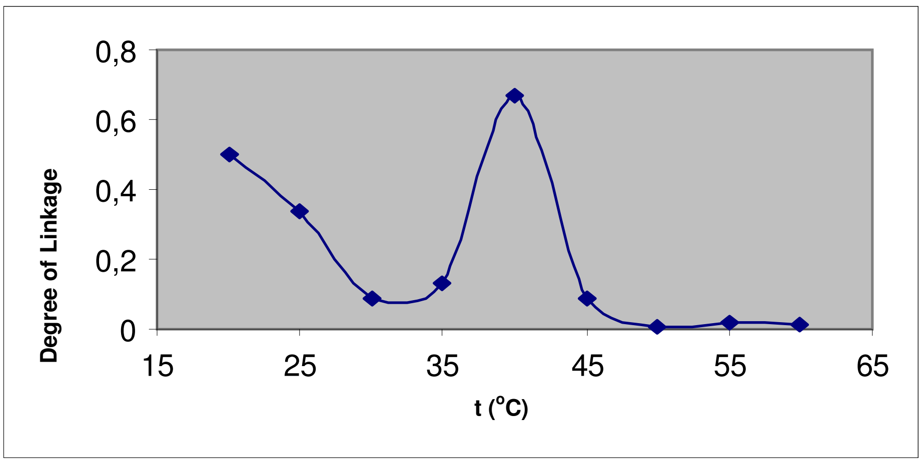

Figure D.86 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

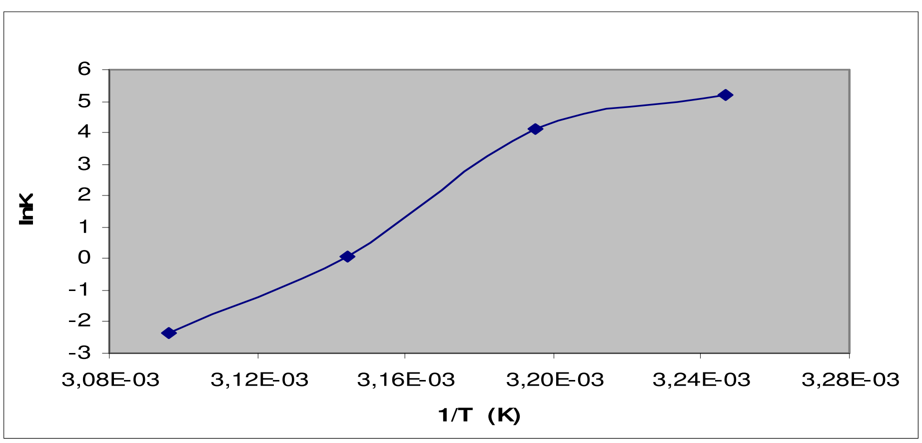

Figure D.87 : Curve of equilibrium constant $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

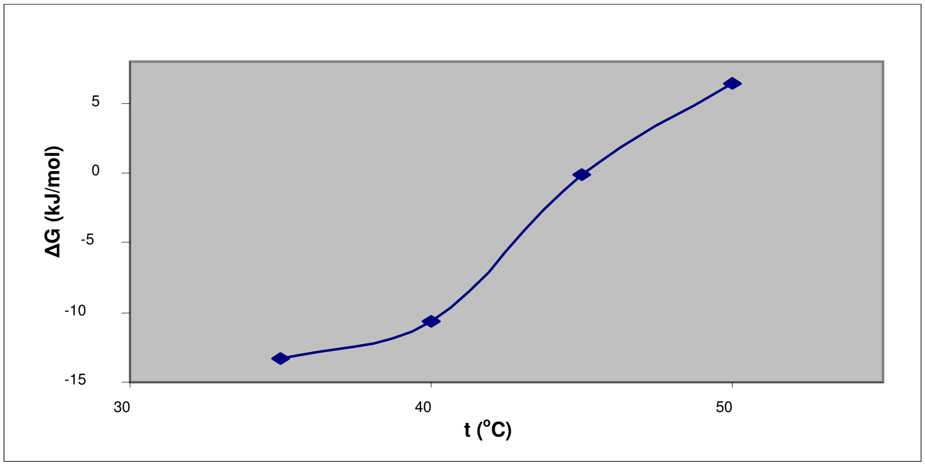

Figure D.88 :$\Delta G = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

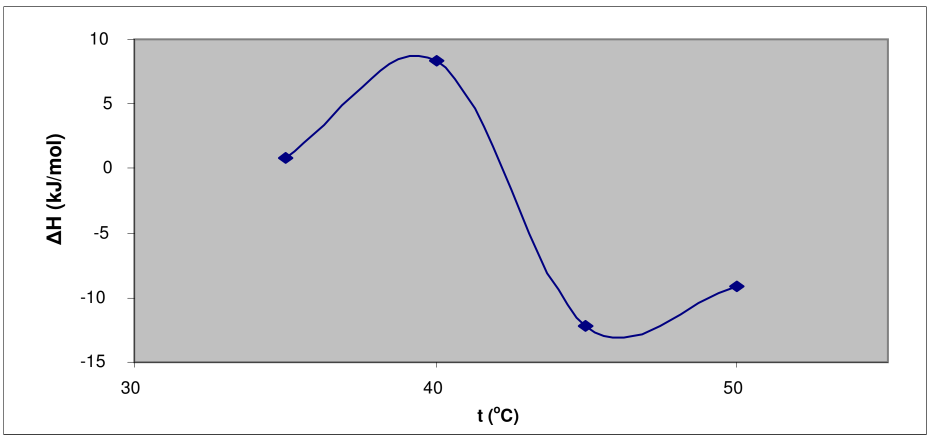

Figure D.89 :$\Delta H = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

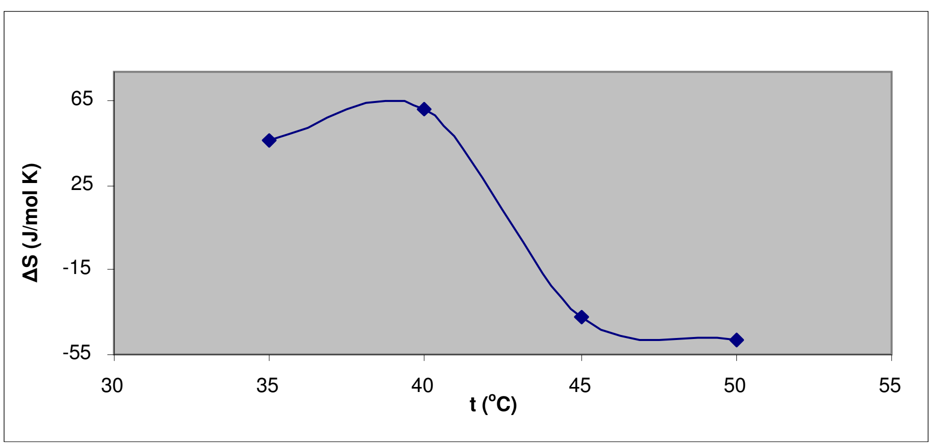

Figure D.90 :$\Delta S = f$ (t˚C) Curve of $1x10^{-1}$(mol/L) PAH- $1x10^{-1}$(mol/L) $CaCl_2$ (I=1 mol/L)

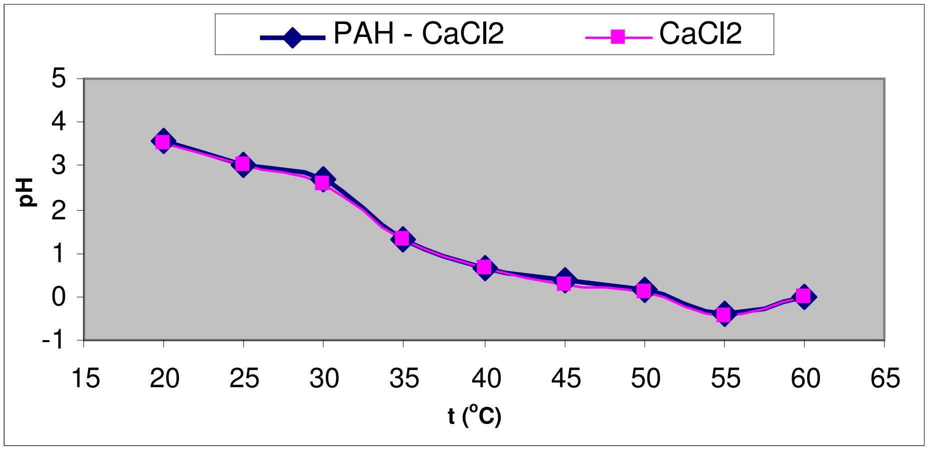

Figure D.91 :pH=*f* (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

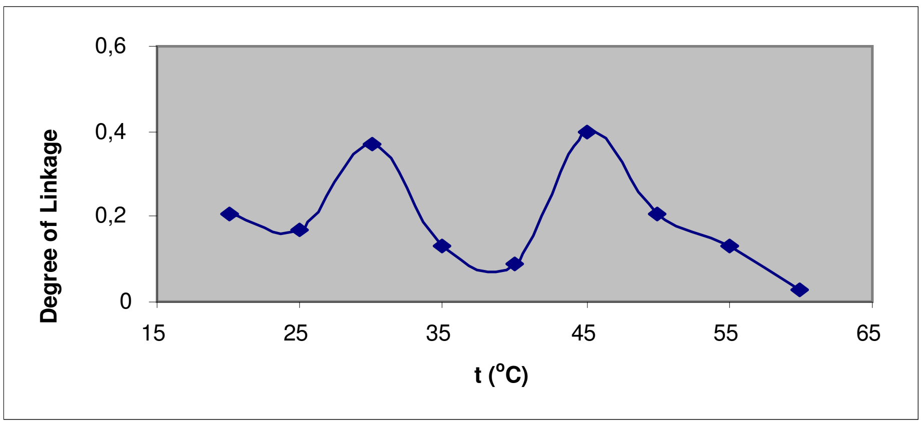

Figure D.92 : Degree of linkage, θ =*f* (t°C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

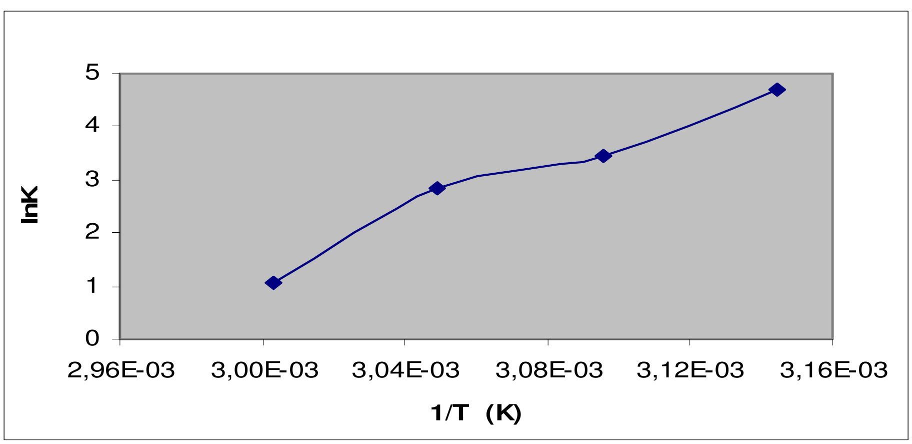

Figure D.93 : Curve of equilibrium constant $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

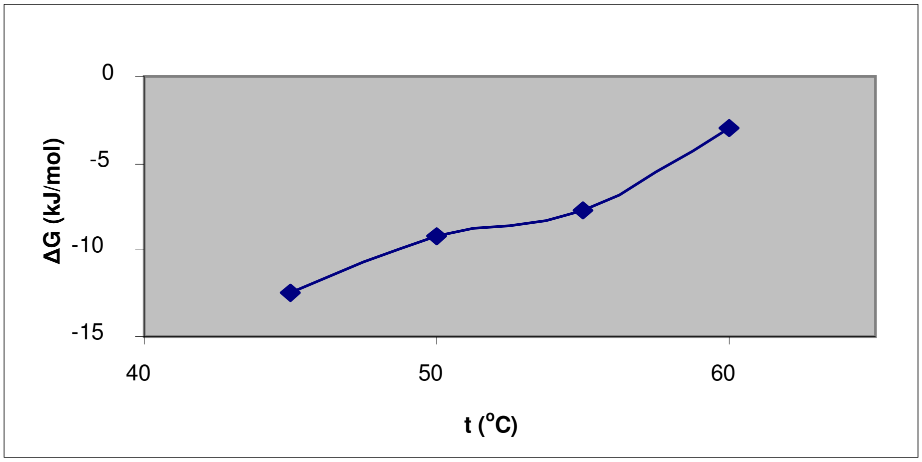

Figure D.94 : $\Delta G = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

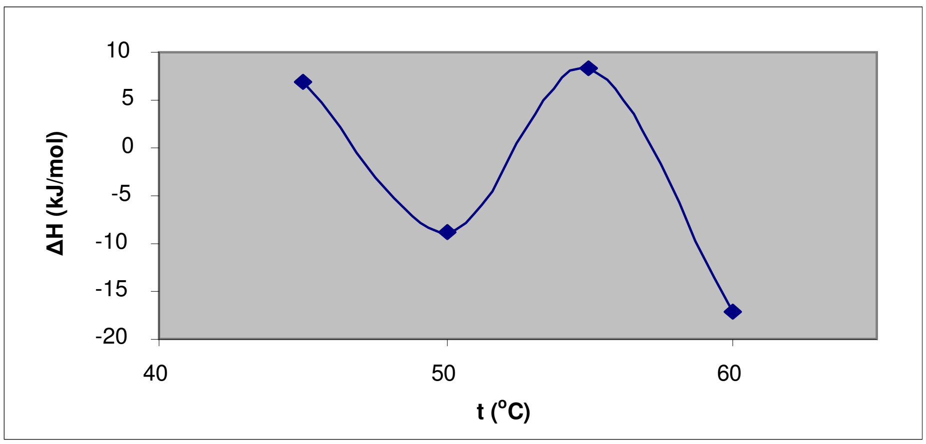

Figure D.95 : $\Delta H = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

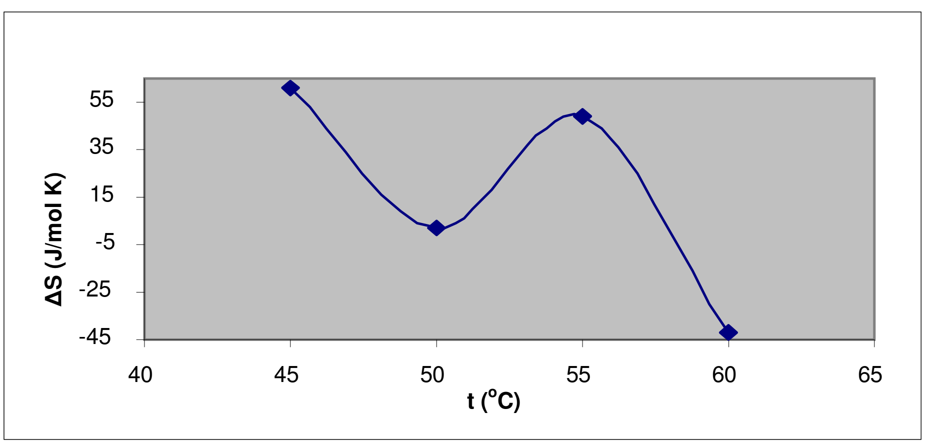

Figure D.96 : $\Delta S = f$ (t˚C) Curve of $1x10^{-2}$(mol/L) PAH- $1x10^{-2}$(mol/L) $CaCl_2$, (I=$1x10^{-1}$ mol/L)

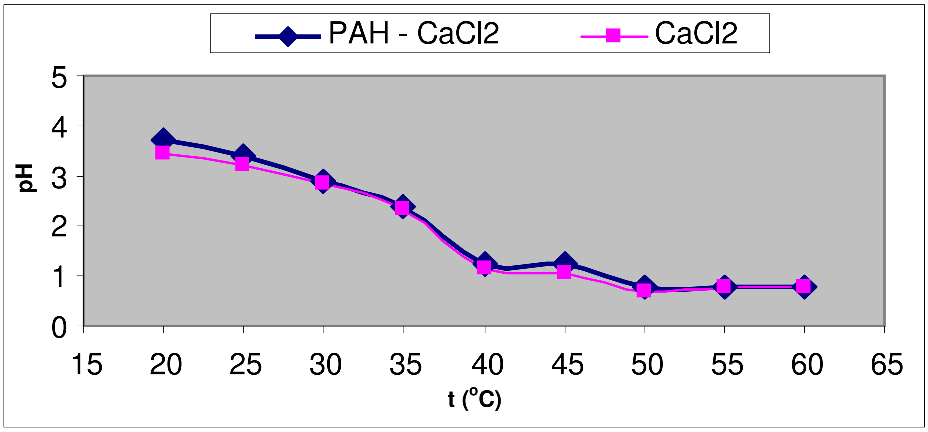

Figure D.97 :pH=*f* (t°C) Curve of 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) $CaCl_2$, (I=1x10^{-2} mol/L)

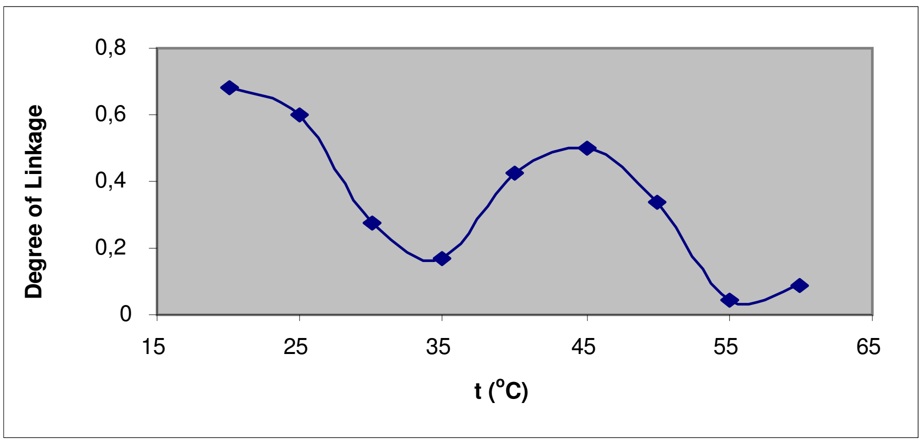

Figure D.98 : Degree of linkage, θ =*f* (t°C) Curve of 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) $CaCl_2$, (I=1x10^{-2} mol/L)

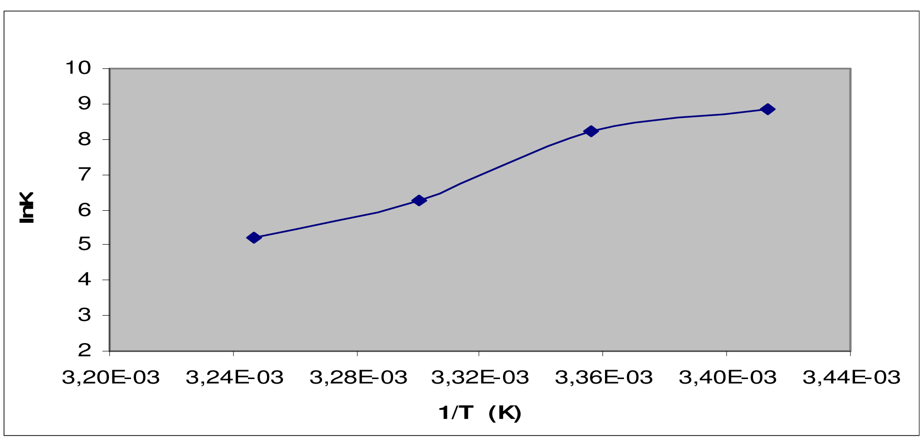

Figure D.99 : Curve of equilibrium constant 1x10^{-3}(mol/L) PAH- 1x10^{-3}(mol/L) $CaCl_2$, (I=1x10^{-2} mol/L)

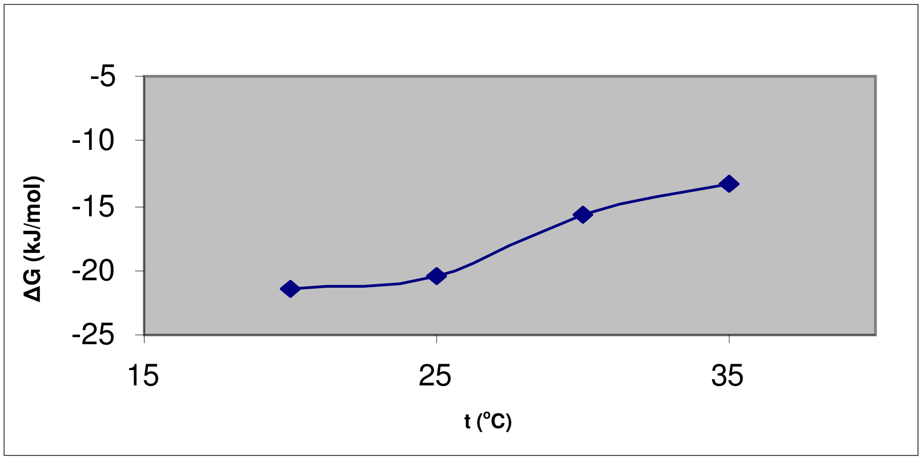

Figure D.100 : $\Delta G = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) $CaCl_2$, ($I=1x10^{-2}$ mol/L)

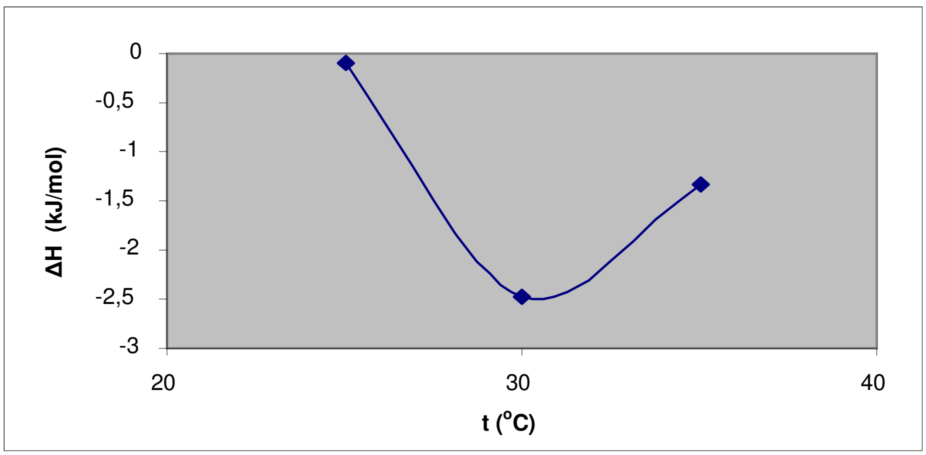

Figure D.101 : $\Delta H = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) $CaCl_2$, ($I=1x10^{-2}$ mol/L)

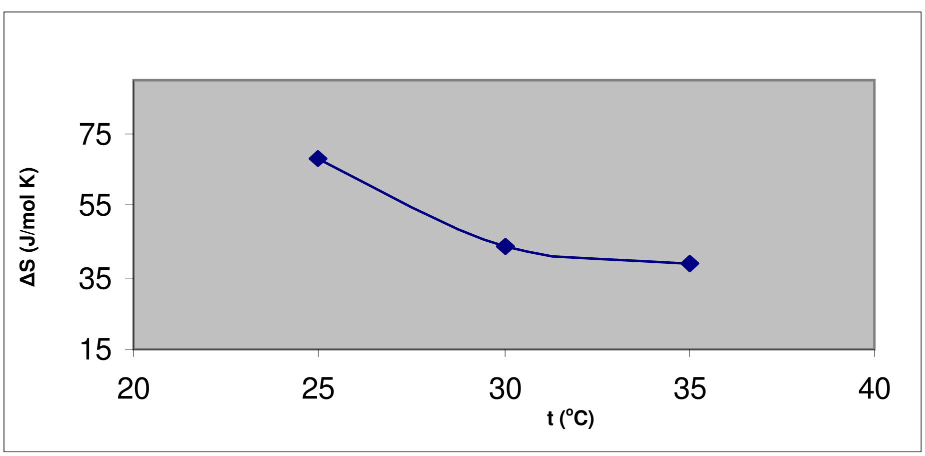

Figure D.102 : $\Delta S = f$ (t°C) Curve of $1x10^{-3}$(mol/L) PAH- $1x10^{-3}$(mol/L) $CaCl_2$, ($I=1x10^{-2}$ mol/L)

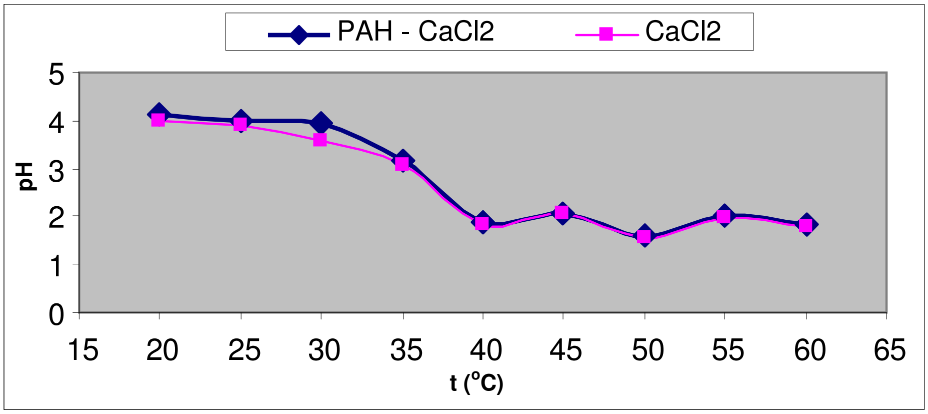

Figure D.103 : pH=f (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, (I=$1x10^{-3}$ mol/L)

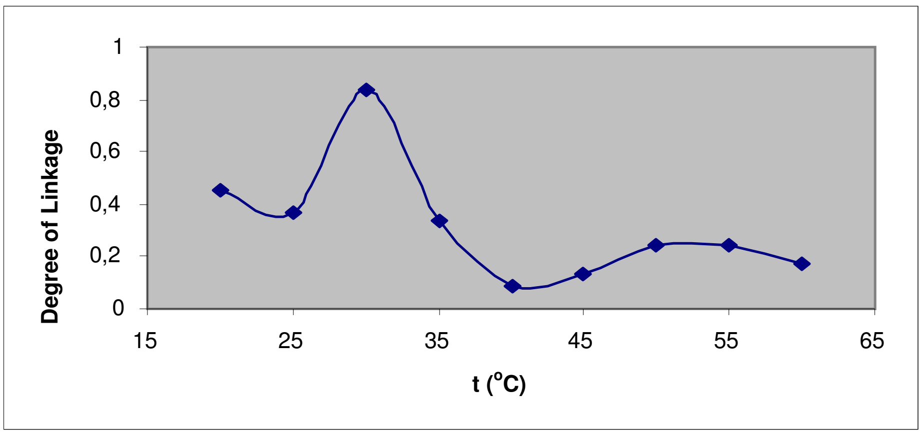

Figure D.104 : Degree of linkage, $\theta = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, (I=$1x10^{-3}$ mol/L)

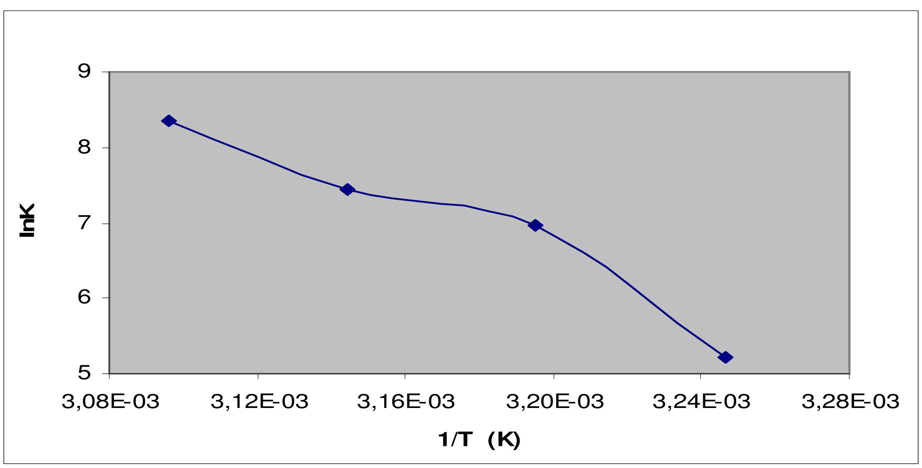

Figure D.105 : Curve of equilibrium constant $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, (I=$1x10^{-3}$ mol/L)

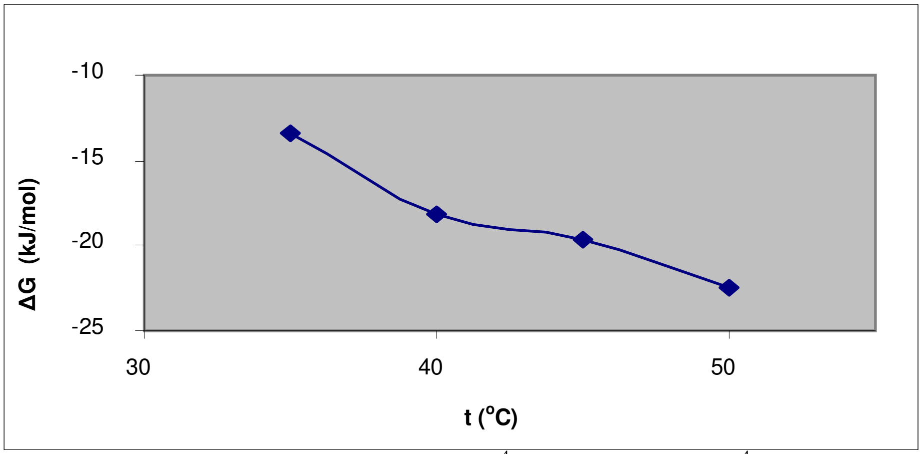

Figure D.106 : $\Delta G = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

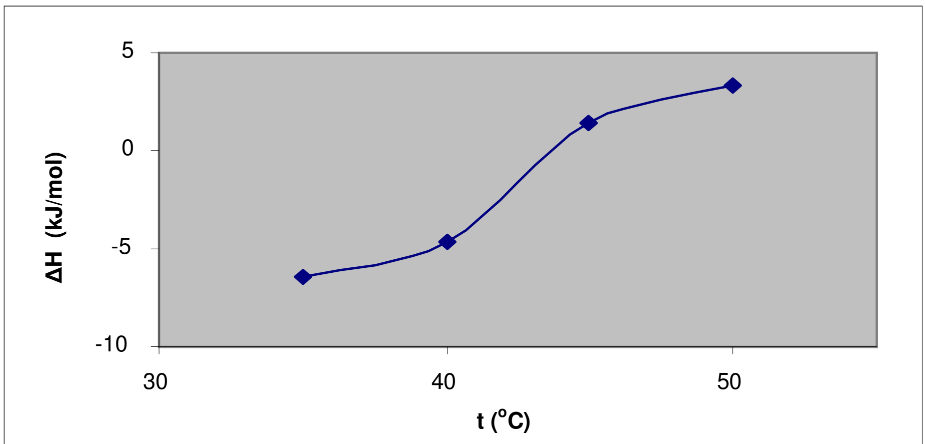

Figure D.107 : $\Delta H = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

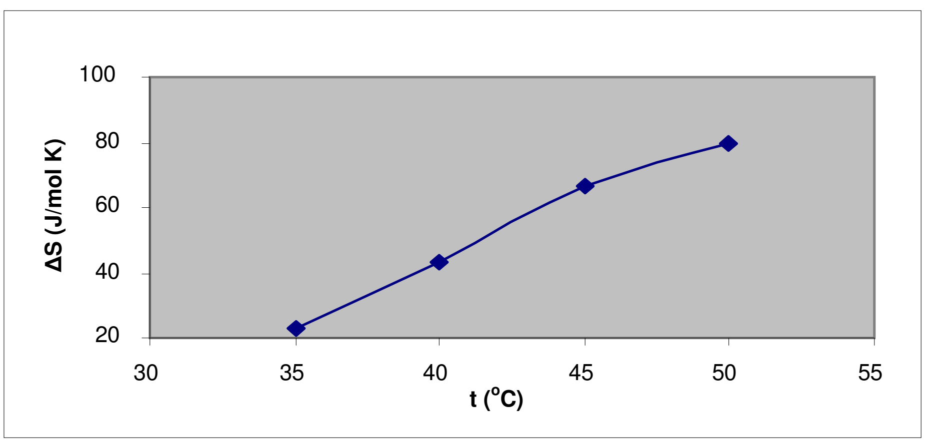

Figure D.108 : $\Delta S = f$ (t°C) Curve of $1x10^{-4}$(mol/L) PAH- $1x10^{-4}$(mol/L) $CaCl_2$, ($I=1x10^{-3}$ mol/L)

APPENDIX E: Table of Thermodynamic Values

Table E.1: Thermodynamic values for PSP – Na_2SO_4 solution (I= varied)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-1}$M PSP-Na_2SO_4	20	0.88	6.41	-15.62		
	25	0.93	7.67	-19.00	182.51	676.21
	30	0.93	7.48	-18.84	-28.69	-32.50
	35	0.83	5.71	-14.63	-273.76	-841.32
	40	0.72	4.56	-11.86	-184.96	-553.02
	45	0.62	3.76	-9.94	-132.55	-385.59
	50	0.67	4.11	-11.04	60.20	220.56
	55	0.79	5.20	-14.18	191.81	628.03
	60	0.68	4.23	-11.70	-177.02	-496.47
$1x10^{-2}$M PSP- Na_2SO_4	20	0.94	10.16	-24.75		
	25	0.94	10.26	-25.41	0.08	85.54
	30	0.92	9.68	-24.40	-0.71	78.16
	35	0.88	8.71	-22.31	-1.69	66.95
	40	0.85	8.22	-21.38	-1.16	64.63
	45	0.85	8.22	-21.73	0.00	68.32
	50	0.89	8.91	-23.93	2.59	82.10
	55	1.00	21.55	-58.77	57.81	355.43
	60	0.96	11.11	-30.75	-57.32	-79.80
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-3}$M PSP- Na_2SO_4	20	0.87	12.08	-29.43		
	25	0.86	10.72	-26.56	-1.13	85.32
	30	0.82	10.11	-25.48	-0.75	81.60
	35	0.65	8.60	-22.02	-2.64	62.92
	40	0.67	8.72	-22.68	0.27	73.33
	45	0.17	5.49	-14.52	-9.64	15.35
	50	0.67	8.72	-23.41	12.06	109.79
	55	0.95	13.03	-35.54	19.73	168.51
	60	0.87	10.92	-30.23	-11.60	55.94
$1x10^{-4}$M PSP- Na_2SO_4	20	0.21	8.09	-19.71		
	25	0.88	13.32	-33.00	4.35	125.32
	30	0.68	11.13	-28.05	-2.73	83.56
	35	0.78	12.00	-30.74	1.52	104.72
	40	0.97	16.55	-43.08	10.59	171.47
	45	1.00	20.54	-54.29	11.92	208.22
	50	0.50	9.90	-26.58	-39.80	-40.96
	55	0.70	11.25	-30.67	6.17	112.30
	60	0.95	15.05	-41.67	20.88	187.84

Table E. 2: Thermodynamic values for PSP – KCl solution (I= varied)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K))
$1x10^{-1}$M PSP-KCl	20	0.75	4.78	-11.64		
	25	0.81	5.41	-13.40	0.52	46.71
	30	0.68	4.23	-10.64	-1.47	30.26
	35	0.48	2.85	-7.29	-2.40	15.87
	40	0.28	1.66	-4.32	-2.77	4.94
	45	0.13	0.53	-1.40	-3.37	-6.19
	50	0.90	6.80	-18.27	23.46	129.19
	55	0.79	5.20	-14.18	-7.33	20.89
	60	0.68	4.23	-11.70	-5.35	19.07
$1x10^{-2}$M PSP-KCl	20	0.92	9.68	-23.59		
	25	0.74	6.97	-17.27	-2.26	50.39
	30	0.58	5.82	-14.65	-1.44	43.60
	35	0.43	4.85	-12.43	-1.68	34.90
	40	0.21	3.48	-9.07	-3.19	18.78
	45	0.21	3.48	-9.21	0.00	28.97
	50	0.58	5.82	-15.62	8.72	75.36
	55	0.96	10.82	-29.52	22.90	159.80
	60	0.99	13.16	-36.43	12.80	147.84
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-3}$M PSP-KCl	20	0.87	10.82	-26.35		
	25	0.62	8.36	-20.72	-2.04	62.68
	30	0.52	7.73	-19.47	-0.79	61.66
	35	0.34	6.66	-17.04	-1.88	49.25
	40	0.98	14.81	-38.54	18.98	183.77
	45	0.73	9.16	-24.23	-16.90	23.06
	50	0.40	7.00	-18.79	-8.10	33.09
	55	0.88	11.02	-30.04	18.37	147.61
	60	0.91	11.50	-31.85	2.68	103.69
$1x10^{-4}$M PSP-KCl	20	0.31	11.47	-27.93		
	25	0.64	10.79	-26.72	-0.57	87.77
	30	0.40	9.30	-23.43	-1.85	71.22
	35	0.37	9.13	-23.39	-0.29	75.00
	40	0.56	10.29	-26.79	2.70	94.22
	45	0.13	7.44	-19.67	-8.55	34.97
	50	0.34	8.96	-24.06	5.68	92.08
	55	0.70	11.25	-30.67	10.46	125.38
	60	0.84	12.72	-35.22	8.10	130.10

Table E. 3: Thermodynamic values for PSP – K_2SO_4 solution (I= varied)

M=mol/L	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-1}$M PSP-K_2SO_4	20	0.56	3.39	-8.25		
	25	0.68	4.23	-10.47	0.70	37.47
	30	0.68	4.23	-10.64	0.00	35.13
	35	0.74	4.67	-11.95	0.77	41.33
	40	0.45	2.70	-7.03	-4.58	7.85
	45	0.21	1.18	-3.12	-4.55	-4.49
	50	0.54	3.26	-8.75	7.77	51.13
	55	0.80	5.30	-14.46	9.36	72.62
	60	0.87	6.21	-17.20	4.99	66.66
$1x10^{-2}$M PSP- K_2SO_4	20	0.93	9.78	-23.82		
	25	0.91	9.40	-23.28	-0.32	77.04
	30	0.89	8.91	-22.45	-0.61	72.08
	35	0.94	10.07	-25.78	2.02	90.24
	40	0.83	7.91	-20.59	-5.01	49.79
	45	0.67	6.41	-16.96	-4.49	39.20
	50	0.56	5.69	-15.28	-2.71	38.91
	55	0.28	3.96	-10.80	14.28	76.46
	60	0.48	5.15	-14.26	-20.09	-17.51
	t°c	**θ**	**lnK**	**ΔG(kJ/mol)**	**ΔH(kJ/mol)**	**ΔS(J/mol°K)**
$1x10^{-3}$M PSP- K_2SO_4	20	0.89	11.11	-27.08		
	25	0.87	10.82	-26.80	-0.25	89.12
	30	0.92	11.89	-29.95	1.34	103.27
	35	0.84	10.42	-26.68	-2.57	78.29
	40	1.00	20.08	-52.25	22.48	238.75
	45	0.74	9.27	-24.52	-32.34	-24.58
	50	0.83	10.32	-27.71	3.91	97.89
	55	0.87	10.92	-29.77	2.74	99.13
	60	0.95	12.84	-35.56	10.56	138.50
$1x10^{-4}$M PSP- K_2SO_4	20	0.50	9.90	-24.11		
	25	0.58	12.72	-31.52	2.35	113.67
	30	0.74	13.88	-34.96	1.44	120.14
	35	0.74	14.09	-36.08	0.00	117.14
	40	0.71	13.65	-35.52	1.96	119.74
	45	0.45	11.91	-31.50	-8.40	72.62
	50	0.34	11.26	-30.24	-2.44	86.07
	55	0.48	12.06	-32.88	3.65	111.37
	60	0.48	12.06	-33.38	0.00	100.25

Table E. 4: Thermodynamic values for PSP – NaCl solution (I= constant)

M=mol/L	$t^o c$	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-1}$M PSP-NaCl (I= 1 M)	20	2.06E-01	15.00	-36.53		
	25	1.83E-02	12.15	-30.11	-2.37	93.09
	30	4.59E-03	10.74	-27.07	-1.75	83.54
	35	1.83E-02	5.22	-13.36	2.46	51.35
	40	9.17E-03	11.44	-29.78	-1.65	89.89
	45	1.83E-02	12.15	-32.13	2.12	107.68
	50	4.59E-03	10.74	-28.85	-5.26	73.03
	55	4.59E-03	10.74	-29.30	0.00	89.33
	60	9.17E-03	11.44	-31.68	3.84	106.69
$1x10^{-2}$M PSP-NaCl (I= $1x10^{-1}$ M)	20	4.50E-01	5.01	-12.19		
	25	8.80E-02	2.36	-5.84	-2.20	12.23
	30	1.29E-01	2.83	-7.14	0.59	25.52
	35	2.06E-01	3.48	-8.92	1.14	32.65
	40	1.37E-02	0.34	-0.90	-7.31	-20.50
	45	3.62E-02	1.36	-3.59	3.04	20.86
	50	1.37E-02	0.34	-0.92	-3.80	-8.90
	55	2.73E-02	1.06	-2.88	3.26	18.75
	60	1.37E-02	0.34	-0.95	-3.92	-8.90
	$t^o c$	**θ**	**lnK**	**ΔG(kJ/mol)**	**ΔH(kJ/mol)**	**ΔS(J/mol°K)**
$1x10^{-3}$M PSP-NaCl (I= $1x10^{-2}$ M)	20	2.41E-01	6.18	-15.05		
	25	2.41E-01	6.04	-14.96	0.00	50.21
	30	2.06E-01	5.79	-14.58	-0.31	47.07
	35	1.68E-01	5.49	-14.07	-0.51	44.01
	40	2.41E-01	6.04	-15.72	1.27	54.27
	45	2.41E-01	6.04	-15.97	0.00	50.21
	50	2.06E-01	5.79	-15.54	-0.94	45.19
	55	4.50E-02	3.90	-10.63	-8.63	6.10
	60	1.68E-01	5.49	-15.21	8.75	71.96
$1x10^{-4}$M PSP-NaCl (I= $1x10^{-3}$ M)	20	3.08E-01	6.18	-15.05		
	25	4.75E-01	6.04	-14.96	0.82	52.96
	30	1.68E-01	5.79	-14.58	-2.44	40.05
	35	4.75E-01	5.49	-14.07	3.42	56.78
	40	5.21E-01	6.04	-15.72	0.64	52.27
	45	6.20E-01	6.04	-15.97	1.90	56.17
	50	3.39E-01	5.79	-15.54	-6.39	28.33
	55	1.68E-01	3.90	-10.63	-5.31	16.22
	60	3.08E-01	5.49	-15.21	5.34	61.72

Table E. 5: Thermodynamic values for PSP – Na_2SO_4 solution (I= constant)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-1}$M PSP- Na_2SO_4 (I= 1 M)	20	1.00E+00	21.92	-53.40		
	25	2.86E-01	1.72	-4.26	-16.79	-42.04
	30	4.08E-01	2.46	-6.19	0.92	23.46
	35	4.70E-01	2.82	-7.22	0.63	25.49
	40	5.63E-01	3.39	-8.81	1.32	32.38
	45	6.30E-01	3.83	-10.13	1.33	36.02
	50	6.44E-01	3.92	-10.54	0.35	33.73
	55	6.35E-01	3.87	-10.54	-0.27	31.32
	60	6.53E-01	4.00	-11.06	0.71	35.35
$1x10^{-2}$M PSP-Na_2SO_4 (I= $1x10^{-1}$ M)	20	3.97E-01	4.70	-11.44		
	25	2.06E-01	3.48	-8.63	-1.01	25.59
	30	1.29E-01	2.97	-7.48	-0.81	22.02
	35	1.29E-01	2.45	-6.27	0.00	20.37
	40	9.17E-03	-0.07	0.18	-6.76	-22.15
	45	2.73E-02	1.06	-2.80	3.37	19.40
	50	2.73E-02	1.06	-2.84	0.00	8.79
	55	9.17E-03	-0.07	0.19	-5.15	-16.27
	60	9.17E-03	-0.07	0.19	0.00	-0.57
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-3}$M PSP- Na_2SO_4 (I= $1x10^{-2}$ M)	20	2.06E-01	5.79	-14.10		
	25	1.29E-01	5.14	-12.73	-0.54	40.89
	30	1.29E-01	5.14	-12.94	0.00	42.70
	35	8.80E-02	4.66	-11.94	-0.83	36.06
	40	4.50E-02	3.90	-10.15	-1.78	26.74
	45	8.80E-02	4.66	-12.32	2.28	45.93
	50	1.68E-01	5.49	-14.75	3.11	55.32
	55	2.41E-01	6.04	-16.47	2.49	57.81
	60	3.08E-01	6.47	-17.91	2.35	60.83
$1x10^{-4}$M PSP- Na_2SO_4 (I= $1x10^{-3}$ M)	20	3.08E-01	6.47	-15.75		
	25	3.39E-01	6.66	-16.49	0.16	55.86
	30	3.08E-01	6.47	-16.29	-0.23	53.00
	35	1.29E-01	5.14	-13.15	-2.32	35.16
	40	4.50E-02	3.90	-10.15	-2.88	23.21
	45	3.08E-01	6.47	-17.10	7.69	77.95
	50	8.80E-02	4.66	-12.52	-6.76	17.84
	55	2.76E-01	6.26	-17.08	7.33	74.41
	60	8.80E-02	4.66	-12.91	-8.79	12.35

Table E. 6: Thermodynamic values for PSP – KCl solution (I= constant)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-2}$ M PSP-KCl (I= $1x10^{-1}$ M)	20	8.80E-02	2.36	-5.75		
	25	1.68E-01	3.19	-7.91	0.69	28.85
	30	8.80E-02	2.36	-5.94	-1.04	16.19
	35	1.29E-01	1.73	-4.43	0.83	17.08
	40	4.59E-03	-0.77	2.00	-8.39	-33.18
	45	1.37E-02	0.34	-0.91	3.33	13.33
	50	9.17E-03	-0.07	0.18	-1.54	-5.35
	55	9.17E-03	-0.07	0.19	0.00	-0.57
	60	1.37E-02	0.34	-0.95	2.26	9.65
$1x10^{-3}$ M PSP-KCl (I= $1x10^{-2}$ M)	20	4.50E-02	3.90	-9.50		
	25	8.80E-02	4.66	-11.55	0.63	40.88
	30	1.68E-01	5.49	-13.84	1.04	49.10
	35	2.41E-01	6.04	-15.46	0.95	53.30
	40	1.68E-01	5.49	-14.30	-1.27	41.62
	45	2.06E-01	5.79	-15.30	0.88	50.87
	50	4.50E-02	3.90	-10.47	-7.06	10.55
	55	2.06E-01	5.79	-15.78	8.63	74.43
	60	9.17E-03	2.23	-6.19	-19.49	-39.97
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-4}$M PSP-KCl (I= $1x10^{-3}$ M)	20	1.68E-01	5.49	-13.38		
	25	2.06E-01	5.79	-14.34	0.24	48.93
	30	2.76E-01	6.26	-15.78	0.59	54.04
	35	2.41E-01	6.04	-15.46	-0.39	48.94
	40	8.80E-02	5.11	-13.30	-3.21	32.24
	45	1.29E-01	5.14	-13.58	1.42	47.17
	50	1.68E-01	5.49	-14.75	1.34	49.81
	55	1.29E-01	5.14	-14.01	-1.63	37.72
	60	1.29E-01	5.14	-14.22	0.00	42.70

Table E. 7: Thermodynamic values for PSP – K_2SO_4 solution (I= constant)

M=mol/L	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-2}$ M PSP-K_2SO_4 (I= $1x10^{-1}$ M)	20	1.68E-01	3.19	-7.77		
	25	2.41E-01	3.74	-9.26	0.45	32.59
	30	8.80E-02	2.36	-5.94	-1.72	13.94
	35	1.29E-01	2.83	-7.26	0.83	26.25
	40	1.68E-01	3.19	-8.30	0.83	29.19
	45	2.69E-01	3.92	-10.36	2.18	39.41
	50	4.19E-01	4.82	-12.95	3.38	50.58
	55	4.59E-03	-0.77	2.10	-25.57	-84.34
	60	9.17E-03	-0.07	0.19	3.84	10.97
$1x10^{-3}$ M PSP- K_2SO_4 (I= $1x10^{-2}$ M)	20	1.29E-01	5.14	-12.51		
	25	1.29E-01	5.14	-12.73	0.00	42.70
	30	1.29E-01	5.14	-12.94	0.00	42.70
	35	1.29E-01	5.14	-13.15	0.00	42.70
	40	1.68E-01	5.49	-14.30	0.83	48.33
	45	4.75E-01	7.45	-19.71	5.86	80.41
	50	3.69E-01	6.83	-18.35	-2.32	49.61
	55	8.80E-02	4.66	-12.71	-9.93	8.50
	60	4.50E-02	3.90	-10.79	-4.18	19.85
	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-4}$ M PSP- K_2SO_4 (I= $1x10^{-3}$ M)	20	8.80E-02	6.96	-16.96		
	25	2.06E-01	8.09	-20.04	0.94	70.39
	30	2.76E-01	8.57	-21.58	0.59	73.18
	35	2.41E-01	8.89	-22.76	-0.39	72.64
	40	8.80E-02	6.96	-18.12	-3.21	47.65
	45	1.29E-01	7.44	-19.67	1.42	66.32
	50	1.68E-01	7.80	-20.94	1.34	68.96
	55	1.29E-01	7.44	-20.29	-1.63	56.87
	60	1.29E-01	7.44	-20.60	0.00	61.85

Table E. 8: Thermodynamic values for PSP- $CaCl_2$ solution (I= constant)

M=mol/L	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-1}$M PSP- $CaCl_2$ (I= 1 M)	20	5.63E-01	3.39	-8.25		
	25	3.08E-01	1.86	-4.61	-1.27	11.23
	30	3.39E-01	1.20	-3.02	0.23	10.75
	35	3.39E-01	0.18	-0.46	0.00	1.50
	40	1.29E-01	0.53	-1.38	-3.54	-6.88
	45	3.97E-01	2.39	-6.33	5.57	37.42
	50	1.68E-01	0.89	-2.39	-5.63	-10.04
	55	8.80E-02	0.06	-0.15	-3.81	-11.14
	60	9.17E-03	-2.37	6.56	-13.32	-59.71
$1x10^{-2}$M PSP- $CaCl_2$ (I= $1x10^{-1}$ M)	20	1.68E-01	3.19	-7.77		
	25	3.69E-01	4.53	-11.22	1.11	41.39
	30	2.41E-01	3.74	-9.41	-0.99	27.80
	35	1.29E-01	5.22	-13.36	-1.58	38.25
	40	2.41E-01	3.74	-9.72	2.10	37.78
	45	9.21E-01	9.59	-25.35	17.51	134.79
	50	8.80E-02	2.36	-6.33	-27.05	-64.12
	55	4.50E-02	1.60	-4.35	-3.49	2.64
	60	8.80E-02	2.36	-6.53	4.18	32.18
	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-3}$M PSP- $CaCl_2$ (I= $1x10^{-2}$ M)	20	5.63E-01	7.97	-19.41		
	25	4.99E-01	7.44	-18.43	0.63	63.98
	30	3.08E-01	6.47	-16.29	-1.40	49.13
	35	1.68E-01	5.31	-13.60	-1.70	38.63
	40	2.06E-01	4.87	-12.67	0.68	42.67
	45	2.76E-01	6.26	-16.56	1.43	56.56
	50	8.80E-02	4.66	-12.52	-5.99	20.20
	55	8.80E-02	4.66	-12.71	0.00	38.76
	60	8.80E-02	4.66	-12.91	0.00	38.76
$1x10^{-4}$M PSP- $CaCl_2$ (I= $1x10^{-3}$ M)	20	2.41E-01	6.04	-14.71		
	25	1.68E-01	5.49	-13.61	-0.45	44.15
	30	2.06E-01	5.31	-13.38	0.37	45.35
	35	4.25E-01	4.60	-11.78	2.39	46.01
	40	5.43E-01	7.86	-20.46	1.64	70.62
	45	8.80E-02	4.66	-12.32	-9.58	8.62
	50	8.80E-02	4.66	-12.52	0.00	38.76
	55	8.80E-02	4.66	-12.71	0.00	38.76
	60	1.29E-01	5.14	-14.22	2.61	50.53

Table E. 9: Thermodynamic values for PAH - NaCl solution (I= constant)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-1}$M PAH- NaCl (I= 1 M)	20	2.76E-01	1.66	-4.04		
	25	3.97E-01	2.39	-5.93	0.61	21.95
	30	2.06E-01	1.18	-2.98	-1.51	4.84
	35	2.06E-01	5.22	-13.36	0.00	43.37
	40	1.29E-01	0.53	-1.38	-1.51	-0.42
	45	6.37E-01	3.88	-10.25	10.02	63.74
	50	3.39E-01	2.05	-5.51	-6.84	-4.11
	55	2.06E-01	1.18	-3.22	-3.97	-2.29
	60	1.13E-01	0.36	-1.00	-4.51	-10.54
$1x10^{-2}$M PAH- NaCl (I= $1x10^{-1}$ M)	20	8.80E-02	2.36	-5.75		
	25	1.68E-01	3.19	-7.91	0.69	28.85
	30	2.06E-01	3.48	-8.78	0.37	30.17
	35	8.80E-02	5.22	-13.36	-1.96	36.99
	40	1.68E-01	3.19	-8.30	1.94	32.72
	45	3.39E-01	4.35	-11.51	3.48	47.13
	50	8.80E-02	2.36	-6.33	-7.46	-3.49
	55	4.25E-01	4.85	-13.24	11.41	75.14
	60	2.06E-01	3.48	-9.65	-7.51	6.40
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-3}$M PAH- NaCl (I= $1x10^{-2}$ M)	20	1.29E-01	5.14	-12.51		
	25	2.41E-01	7.49	-18.56	0.75	64.79
	30	4.25E-01	6.60	-16.63	1.39	59.47
	35	1.68E-01	5.22	-13.36	-2.90	33.95
	40	8.80E-02	4.66	-12.13	-1.94	32.56
	45	3.08E-01	6.47	-17.10	5.41	70.77
	50	8.80E-02	4.66	-12.52	-6.76	17.84
	55	3.97E-01	7.00	-19.08	10.69	90.76
	60	1.68E-01	5.49	-15.21	-8.26	20.89
$1x10^{-4}$M PAH- NaCl (I= $1x10^{-3}$ M)	20	4.50E-02	6.20	-15.11		
	25	2.41E-01	8.34	-20.67	1.78	75.32
	30	2.76E-01	8.57	-21.58	0.28	72.14
	35	3.08E-01	5.22	-13.36	0.36	44.53
	40	2.76E-01	8.57	-22.29	-0.47	69.70
	45	6.69E-01	11.02	-29.13	7.34	114.69
	50	7.60E-01	11.79	-31.66	2.89	106.98
	55	3.97E-01	9.30	-25.36	-11.39	42.61
	60	1.68E-01	7.80	-21.58	-8.26	40.03

Table E. 10: Thermodynamic values for PAH – Na_2SO_4 solution (I= constant)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-1}$M PAH- Na_2SO_4 (I= 1 M)	20	6.20E-01	3.76	-9.16		
	25	2.76E-01	1.66	-4.11	-1.75	7.93
	30	2.06E-01	1.18	-2.98	-0.59	7.86
	35	8.80E-02	5.22	-13.36	-1.96	36.99
	40	1.29E-01	0.53	-1.38	1.11	7.95
	45	1.68E-01	0.89	-2.35	1.07	10.75
	50	1.29E-01	0.32	-0.86	-1.34	-1.48
	55	1.83E-02	-1.50	4.09	-10.04	-43.08
	60	1.37E-02	-1.96	5.42	-1.62	-21.14
$1x10^{-2}$M PAH- Na_2SO_4 (I= $1x10^{-1}$ M)	20	6.02E-01	5.94	-14.47		
	25	4.25E-01	4.85	-12.03	-0.90	37.32
	30	6.98E-01	6.64	-16.73	2.23	62.56
	35	1.29E-01	5.22	-13.36	-6.65	21.79
	40	1.29E-01	2.83	-7.37	0.00	23.56
	45	1.29E-01	2.83	-7.49	0.00	23.56
	50	8.80E-02	2.36	-6.33	-1.78	14.11
	55	2.41E-01	3.74	-10.19	6.30	50.27
	60	1.83E-02	0.64	-1.77	-17.00	-45.74
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-3}$M PAH- Na_2SO_4 (I= $1x10^{-2}$ M)	20	2.41E-01	6.04	-14.71		
	25	1.68E-01	5.49	-13.61	-0.45	44.15
	30	8.80E-02	4.66	-11.74	-1.04	35.33
	35	8.80E-02	4.66	-11.94	0.00	38.76
	40	8.80E-02	4.66	-12.13	0.00	38.76
	45	4.25E-01	7.16	-18.92	7.47	82.98
	50	6.20E-01	8.36	-22.46	4.52	83.52
	55	4.50E-01	7.31	-19.93	-4.83	46.03
	60	8.00E-01	9.91	-27.43	14.27	125.25
$1x10^{-4}$M PAH- Na_2SO_4 (I= $1x10^{-3}$ M)	20	7.80	7.80	-18.99		
	25	6.96	6.96	-17.25	-0.69	55.58
	30	8.57	8.57	-21.58	2.00	77.81
	35	5.22	5.22	-13.36	-0.83	40.67
	40	6.20	6.20	-16.14	-4.39	37.52
	45	8.34	8.34	-22.05	10.20	101.42
	50	8.96	8.96	-24.06	-2.44	66.93
	55	7.44	7.44	-20.29	-6.95	40.67
	60	8.34	8.34	-23.09	4.95	84.23

Table E. 11: Thermodynamic values for PAH – KCl solution (I= constant)

M=mol/L	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-2}$ M PSP-KCl (I= $1x10^{-1}$ M)	20	6.02E-01	5.94	-14.47		
	25	5.63E-01	5.69	-14.10	-0.21	46.60
	30	1.29E-01	2.83	-7.14	-3.56	11.81
	35	8.80E-02	5.22	-13.36	-0.83	40.68
	40	1.68E-01	3.19	-8.30	1.94	32.72
	45	8.80E-02	2.00	-5.29	-2.49	8.79
	50	1.29E-01	2.83	-7.61	1.78	29.06
	55	3.39E-01	4.35	-11.87	6.95	57.38
	60	7.25E-01	6.86	-19.00	13.77	98.39
$1x10^{-3}$ M PSP- KCl (I= $1x10^{-2}$ M)	20	1.68E-01	5.49	-13.38		
	25	4.50E-02	3.90	-9.66	-0.30	31.43
	30	3.08E-01	5.12	-12.90	1.66	48.05
	35	2.41E-01	5.55	-14.21	-0.75	43.71
	40	5.21E-01	7.73	-20.12	3.94	76.84
	45	5.83E-01	8.12	-21.46	1.16	71.15
	50	2.76E-01	6.26	-16.82	-6.94	30.59
	55	1.68E-01	7.31	-19.93	4.77	75.31
	60	3.08E-01	7.31	-20.23	0.00	60.76
	t^oc	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol^{o}K)
$1x10^{-4}$ M PSP- KCl (I= $1x10^{-3}$ M)	20	3.39E-01	8.96	-21.82		
	25	1.68E-01	7.80	-19.32	-0.97	61.58
	30	3.08E-01	8.77	-22.09	1.21	76.92
	35	7.60E-01	5.22	-13.36	5.27	60.50
	40	3.69E-01	9.13	-23.77	-6.18	56.19
	45	6.37E-01	10.79	-28.52	4.94	105.21
	50	4.99E-01	9.90	-26.58	-3.33	71.98
	55	3.69E-01	9.13	-24.91	-3.48	65.32
	60	2.41E-01	8.34	-23.09	-0.97	66.44

Table E. 12: Thermodynamic values for PAH – K_2SO_4 solution (I= constant)

M=mol/L	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-2}$M PAH- K_2SO_4 (I= $1x10^{-1}$ M)	20	1.68E-01	3.19	-7.77		
	25	2.76E-01	4.00	-9.91	1.63	38.72
	30	3.69E-01	4.53	-11.41	-0.77	35.10
	35	8.80E-02	5.22	-13.36	-3.79	31.07
	40	1.29E-01	2.83	-7.37	1.11	27.09
	45	8.80E-02	2.36	-6.24	-1.42	15.14
	50	1.29E-01	2.83	-7.61	1.78	29.06
	55	1.68E-01	3.19	-8.70	1.63	31.51
	60	4.50E-02	1.60	-4.42	-8.75	-13.01
$1x10^{-3}$M PAH- K_2SO_4 (I= $1x10^{-2}$ M)	20	4.50E-02	3.90	-9.50		
	25	2.41E-01	6.04	-14.96	1.78	56.18
	30	1.29E-01	5.14	-12.94	-1.13	38.99
	35	4.50E-01	5.22	-13.36	3.79	55.68
	40	1.29E-01	5.14	-13.37	-5.05	26.56
	45	2.41E-01	6.04	-15.97	2.70	58.71
	50	4.50E-02	3.88	-10.42	-3.38	21.80
	55	1.68E-01	5.49	-14.98	1.63	50.66
	60	4.32E-01	7.20	-19.93	7.34	81.91
	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-4}$M PAH- K_2SO_4 (I= $1x10^{-3}$ M)	20	4.50E-02	6.20	-15.11		
	25	2.41E-01	8.34	-20.67	1.78	75.32
	30	8.80E-02	6.96	-17.54	-1.72	52.23
	35	3.39E-01	5.22	-13.36	3.48	54.68
	40	8.80E-02	9.61	-25.01	1.52	84.75
	45	8.90E-01	10.17	-26.88	1.66	89.74
	50	3.39E-01	8.96	-24.06	-4.52	60.50
	55	2.76E-01	8.57	-23.36	-1.79	65.75
	60	1.29E-01	7.44	-20.60	-6.18	43.27

Table E. 13: Thermodynamic values for PAH–$CaCl_2$ solution (I= constant)

M=mol/L	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-1}$M PAH- $CaCl_2$ (I= 1 M)	20	4.99E-01	2.99	-7.28		
	25	3.39E-01	2.05	-5.08	-0.78	14.43
	30	8.80E-02	0.06	-0.14	-2.49	-7.74
	35	1.29E-01	5.22	-13.36	0.83	46.06
	40	6.69E-01	4.11	-10.70	8.33	60.80
	45	8.80E-02	0.06	-0.15	-12.14	-37.70
	50	9.17E-03	-2.37	6.37	-9.08	-47.83
	55	1.83E-02	-1.66	4.54	3.23	-3.98
	60	1.37E-02	-1.96	5.42	-1.62	-21.14
$1x10^{-2}$M PAH- $CaCl_2$ (I= $1x10^{-1}$ M)	20	2.06E-01	3.48	-8.49		
	25	1.68E-01	3.19	-7.91	-0.24	25.71
	30	3.69E-01	4.53	-11.41	1.67	43.16
	35	1.29E-01	5.22	-13.36	-2.96	33.76
	40	8.80E-02	2.36	-6.14	-1.11	16.08
	45	3.97E-01	4.70	-12.41	6.99	61.03
	50	2.06E-01	3.44	-9.24	-8.74	1.53
	55	1.29E-01	2.84	-7.74	8.26	48.79
	60	2.73E-02	1.06	-2.93	-17.05	-42.40
	t°c	θ	lnK	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol°K)
$1x10^{-3}$M PAH- $CaCl_2$ (I= $1x10^{-2}$ M)	20	6.84E-01	8.83	-21.51		
	25	6.02E-01	8.24	-20.42	-0.10	68.19
	30	2.76E-01	6.26	-15.78	-2.47	43.93
	35	1.68E-01	5.22	-13.36	-1.34	39.01
	40	4.25E-01	7.16	-18.62	3.87	71.86
	45	4.99E-01	7.59	-20.08	1.31	67.25
	50	3.39E-01	6.66	-17.87	-3.51	44.47
	55	4.50E-02	3.90	-10.63	-12.61	-6.02
	60	8.80E-02	4.66	-12.91	4.18	51.32
$1x10^{-4}$M PAH- $CaCl_2$ (I= $1x10^{-3}$ M)	20	4.50E-01	9.61	-23.41		
	25	3.69E-01	9.13	-22.63	-0.40	74.62
	30	8.34E-01	12.62	-31.79	4.35	119.28
	35	3.39E-01	5.22	-13.36	-6.39	22.61
	40	8.80E-02	6.96	-18.11	-4.64	43.03
	45	1.29E-01	7.44	-19.67	1.42	66.32
	50	2.41E-01	8.34	-22.40	3.38	79.81
	55	2.41E-01	8.34	-22.75	0.00	69.35
	60	1.68E-01	7.80	-21.58	-2.99	55.83

APPENDIX F: IR spectrums of PSP, PAH, PSP-Salt, and PAH-salt

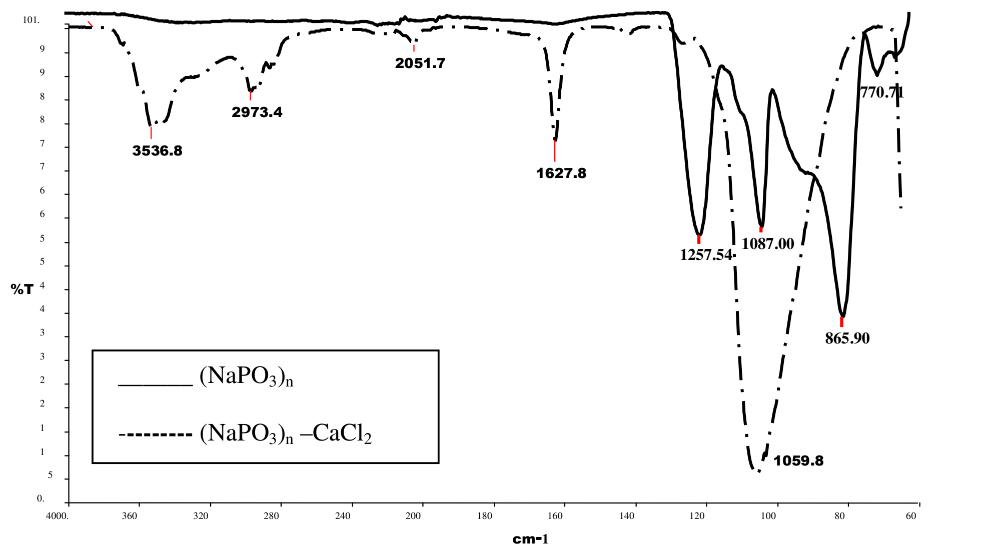

Figure F.1: IR spectrum $1x10^{-2}$ (mol/L) PSP + $1x10^{-2}$ (mol/L) $CaCl_2$ ($I=1x10^{-1}$ mol/L)

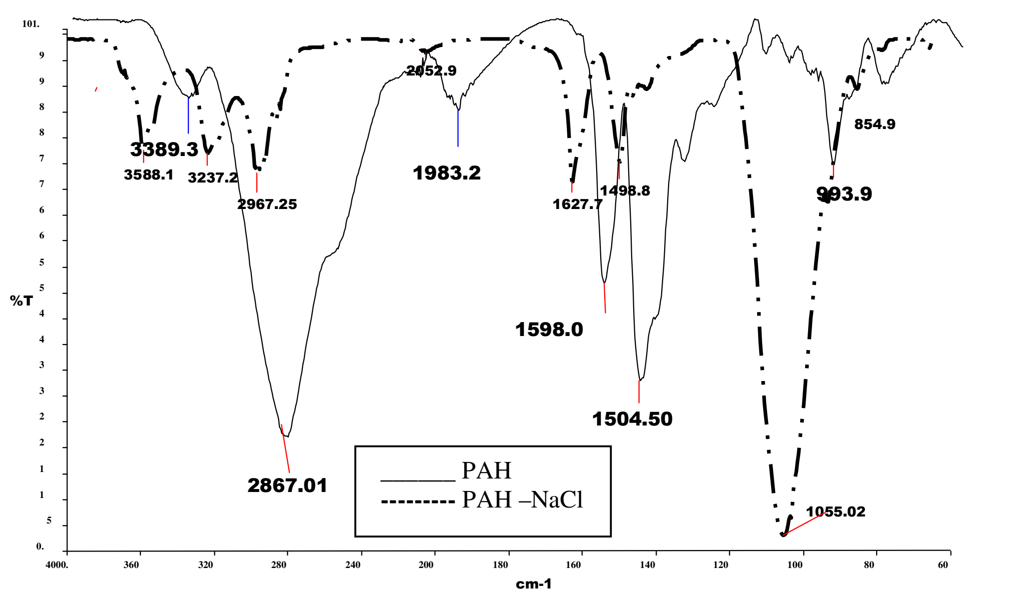

Figure F. 2: IR spectrum $1x10^{-2}$ (mol/L)PAH + $1x10^{-2}$ (mol/L)NaCl, ($I=1x10^{-1}$ mol/L)

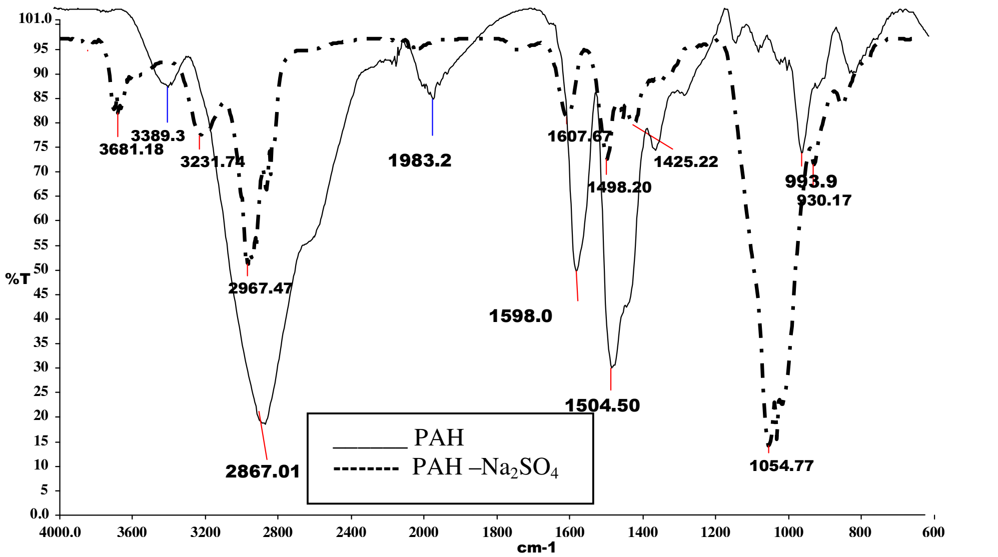

Figure F. 3: IR spectrum $1x10^{-2}$ (mol/L)PAH +$1x10^{-2}$ (mol/L)Na_2SO_4, (I=$1x10^{-1}$ mol/L)

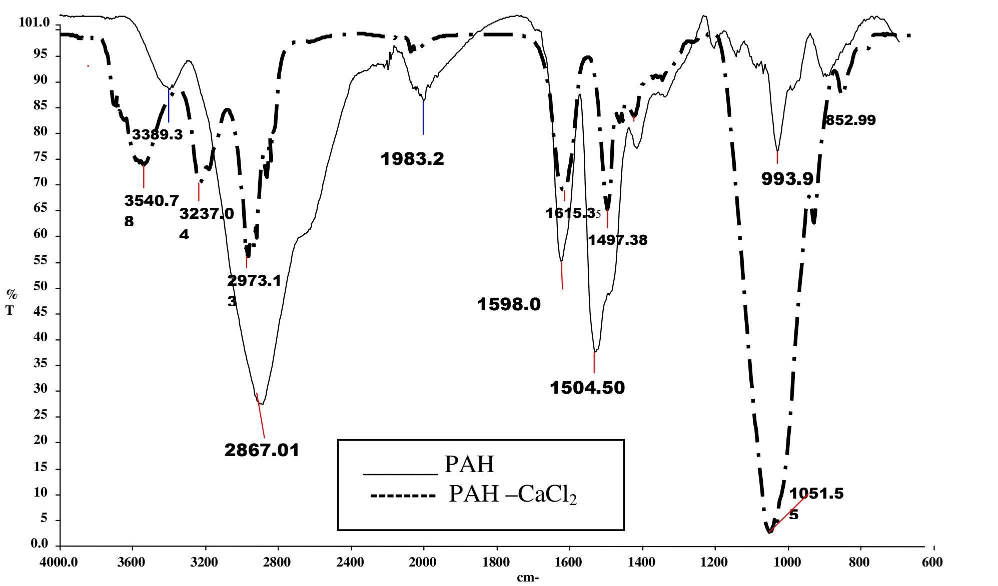

Figure F. 4: IR spectrum $1x10^{-2}$ (mol/L)PAH + $1x10^{-2}$ (mol/L)$CaCl_2$, (I=$1x10^{-1}$ mol/L)

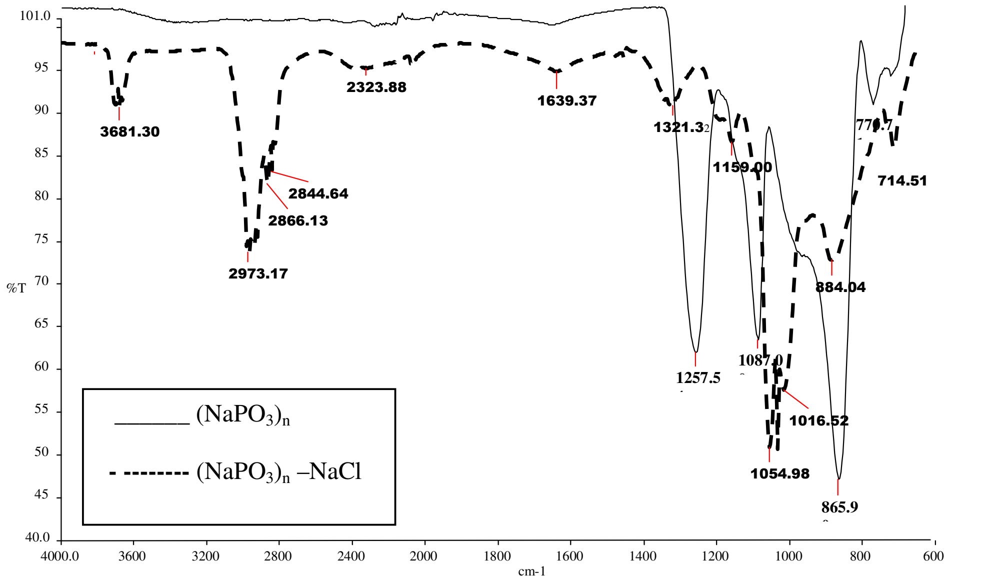

Figure F. 5: IR spectrum $1x10^{-2}$ (mol/L) PSP + $1x10^{-2}$ (mol/L) NaCl

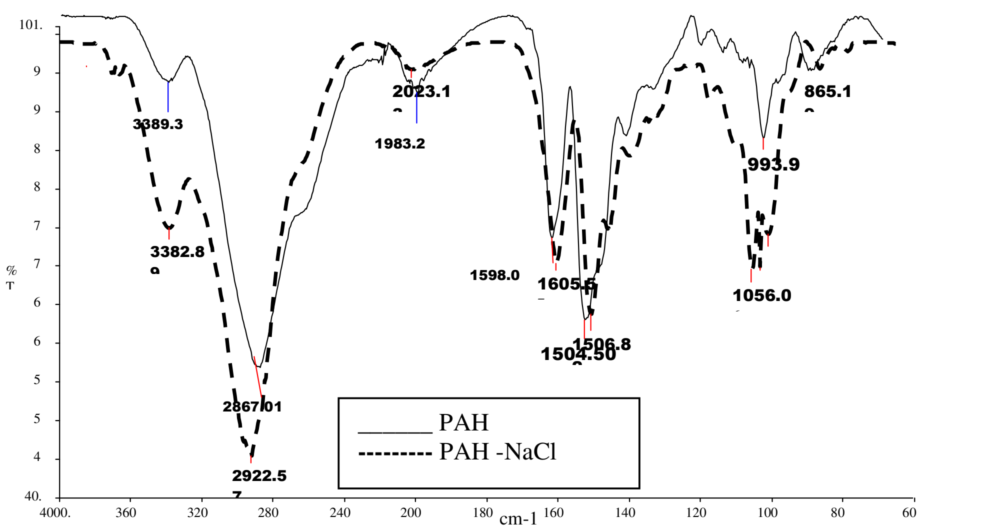

Figure F. 6: IR spectrum $1x10^{-2}$ (mol/L) PAH + $1x10^{-2}$ (mol/L) NaCl

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